Supplementary Material

A Lowly Populated, Transient β-sheet Structure in Monomeric $A\beta^{1-42}$ Identified by Multinuclear NMR of Chemical Denaturation

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Details of urea concentration quantification

The ^{2}H resonances observed in a spectrum of a sample containing 2% D_2O as lock signal was used for urea quantification. This avoids potential interference from ^{1}H radiation damping effects that impact the ^{1}H spectrum. As an example, the exact concentration of a solution after addition of 71.9 mg urea to 425 µL buffer for making a ca. 2.7 M urea concertation is described here. First, the integral ratio of urea to water ($I_{r,urea}$) was obtained to be 0.1127 from fitting the ^{2}H spectrum to Gaussian-Lorentzian functions (Figure S1). The fitting was performed using the line shape fitting tool implemented in the TopSpin software. From $I_{r,urea}$, the weight ratio ($W_{r,urea}$) was then calculated using the following formula:

$$W_{r.urea} = \frac{60.06 \times I_{r.urea}}{2 \times 18.02} = 0.187812$$

in which 60.06 and 18.02 g/mol are the molecular weights of urea and water respectively and the factor 2 reflects the ratio of their number of hydrogens per molecule. Then, the above $W_{r,urea}$ value was converted to the urea weight fraction ($W_{f,urea}$):

$$W_{f.urea} = \frac{1}{1 + 1/W_{r.urea}} = 0.15811$$

from $W_{f,urea}$, the density of the solution (d) was calculated using the relationship reported by Kawahara and Tanford:[1]

$$d = 0.997 \times (1 + 0.2658\, W_{f.urea} + 0.0330\, W_{f.urea}^{2})$$

With D_{sol} and $W_{f,urea}$ in hand, the number of moles of urea in 1000 mL solution, i.e. the urea molarity [U] was derived from:

$$[U] = 1000\ \text{mL solution} \times \frac{d\ \text{g solution}}{1\ \text{mL solution}} \times \frac{W_{f.urea}\ \text{g urea}}{1\ \text{g solution}} \times \frac{1\ \text{mol urea}}{60.06\ \text{g urea}} = 2.737\ \text{M}$$

Figures

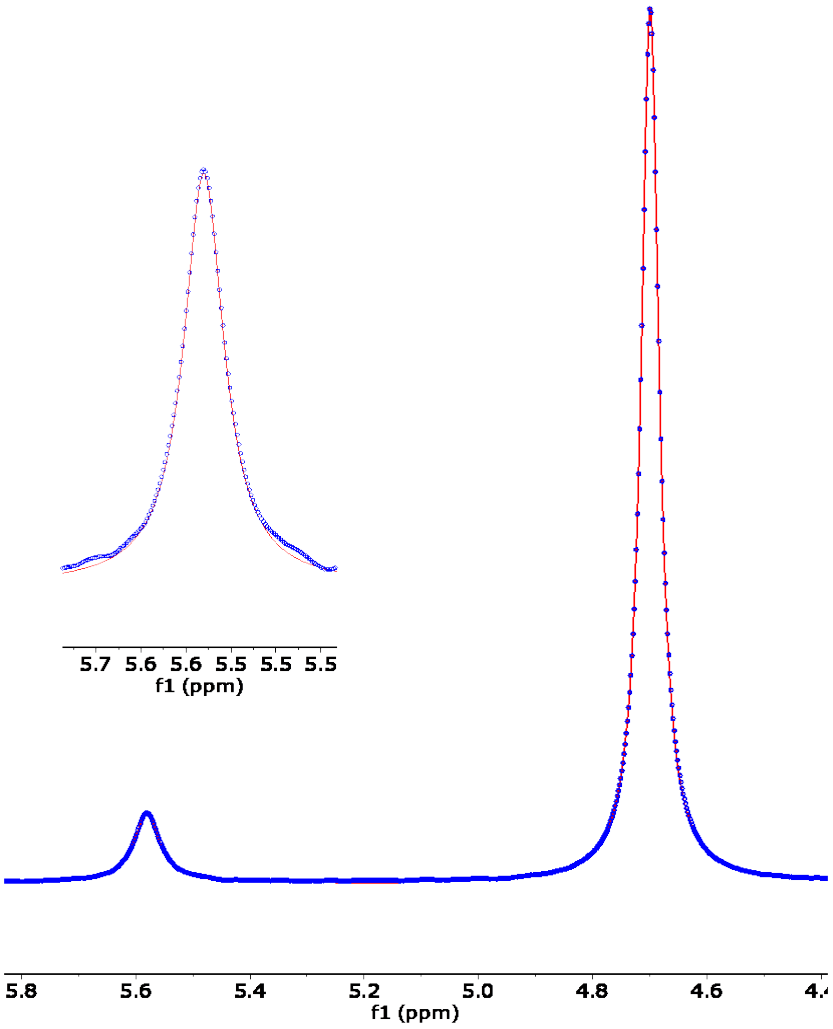


Figure S1. Example of a ^{2}H spectrum used for urea quantification. The blue circles show the experimental spectrum and the red line is the best Gaussian-Lorentzian fit. Peaks at ca. 4.7 and 5.6 ppm correspond to water and urea respectively. The spectrum was collected at 278 K after addition of 71.9 mg urea to ca. 425 μL of sample.

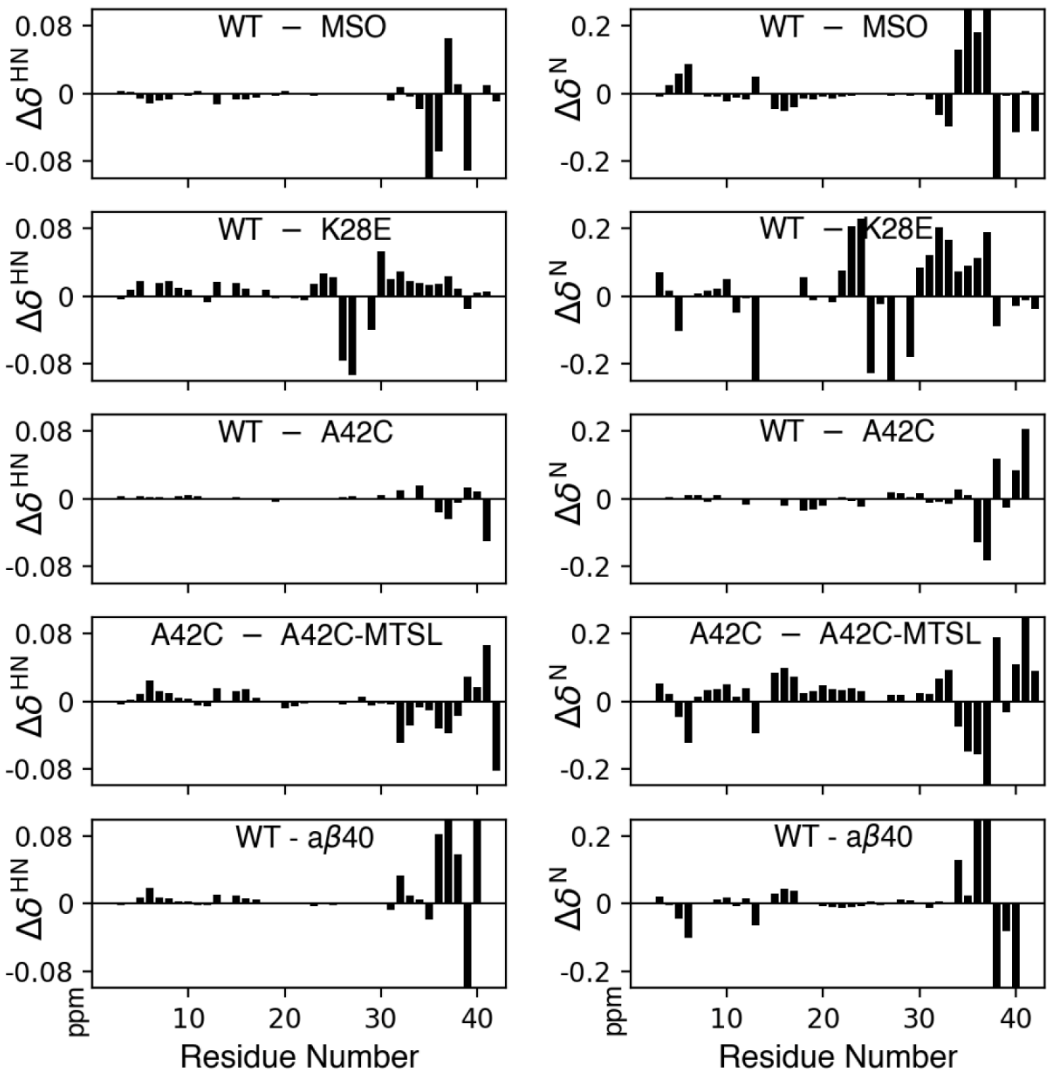


Figure S2. $^{1}H^{N}$ and ^{15}N chemical shift differences between Aβ variants. From top to bottom, plotted are the chemical shift differences between wild-type $A\beta^{1-42}$ (WT) and its Met-35 oxidized form (MSO); between WT and the K28E mutant; between WT and its A42C (free sulfhydryl) mutant; between A42C and its MTSL-tagged form, after reduction with ascorbate; between WT and $A\beta^{1-40}$. All spectra were in 44 mM Tris-HCl, 10 mM NaCl, 2 mM EDTA, 278 K, pH nominally 7.4 (but see Figure S3).

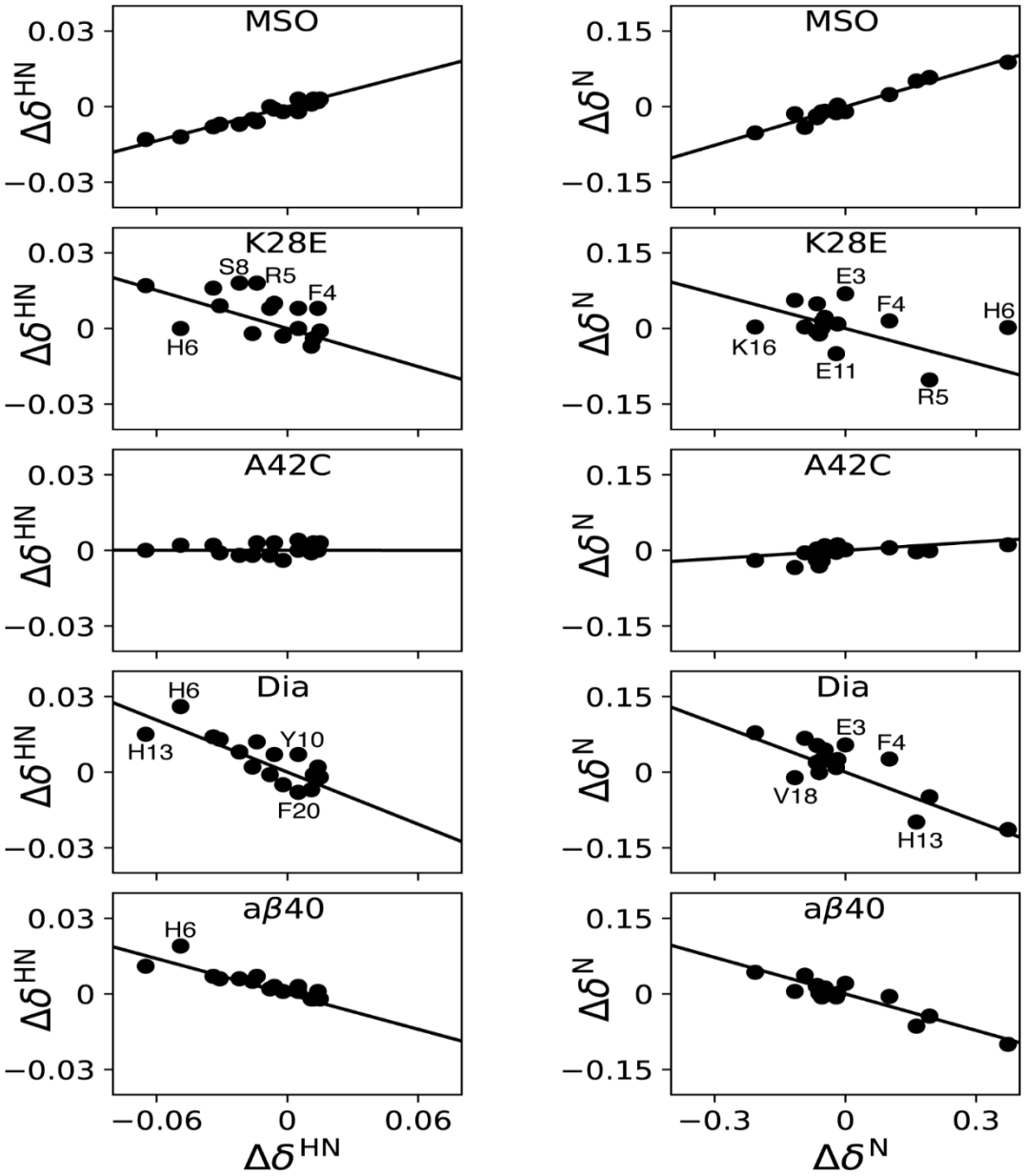


Figure S3. Correlations of the pH dependence of $A\beta^{1-42}$ NMR chemical shifts and the chemical shift differences of Figure S2, for the N-terminal 20 residues of Aβ and its variants. The horizontal axis corresponds to the chemical shift difference between WT $A\beta^{1-42}$ at pH values of pH 7.4 and 6.8 (glass electrode reading at room temperature). The y-axis displays the measured chemical shift differences between WT $A\beta^{1-42}$ and the variants displayed in Figure S2, 44 mM Tris-HCl, 10 mM NaCl, 2 mM EDTA, 278 K, pH nominally 7.4. Top to bottom: Met-35 oxidized; K28E; A42C; A42C-MTSL (reduced); $A\beta^{1-40}$. Chemical shift differences for residues close to the fitted lines are dominated by small pH deviations from the nominal value of 7.4. Outliers reflect residues that contain a pH-independent contribution.

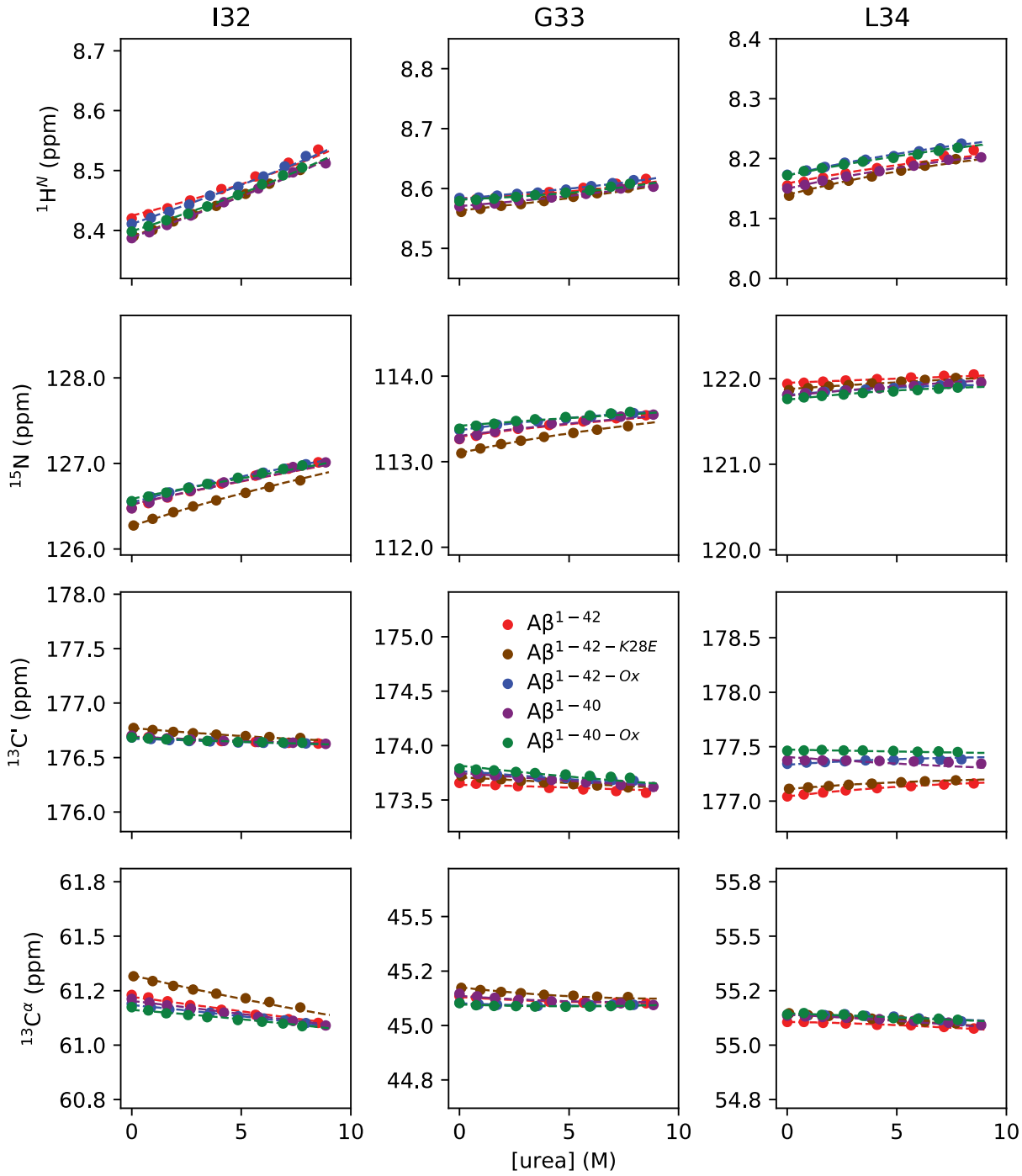


Figure S4. Urea titrations of the backbone chemical shifts of residues I32-V36 and V40-A42 in five Aβ peptides. Curves for G37-V39 are shown Figure 3 of the main text. Dashed lines correspond to fits to eq (5), using global $\boldsymbol{m}$ and $\boldsymbol{A}$ values across residues I32-I41 (I32-V39 for $A\beta^{1\text{-}40}$).

Figure S4 -CONTINUED-

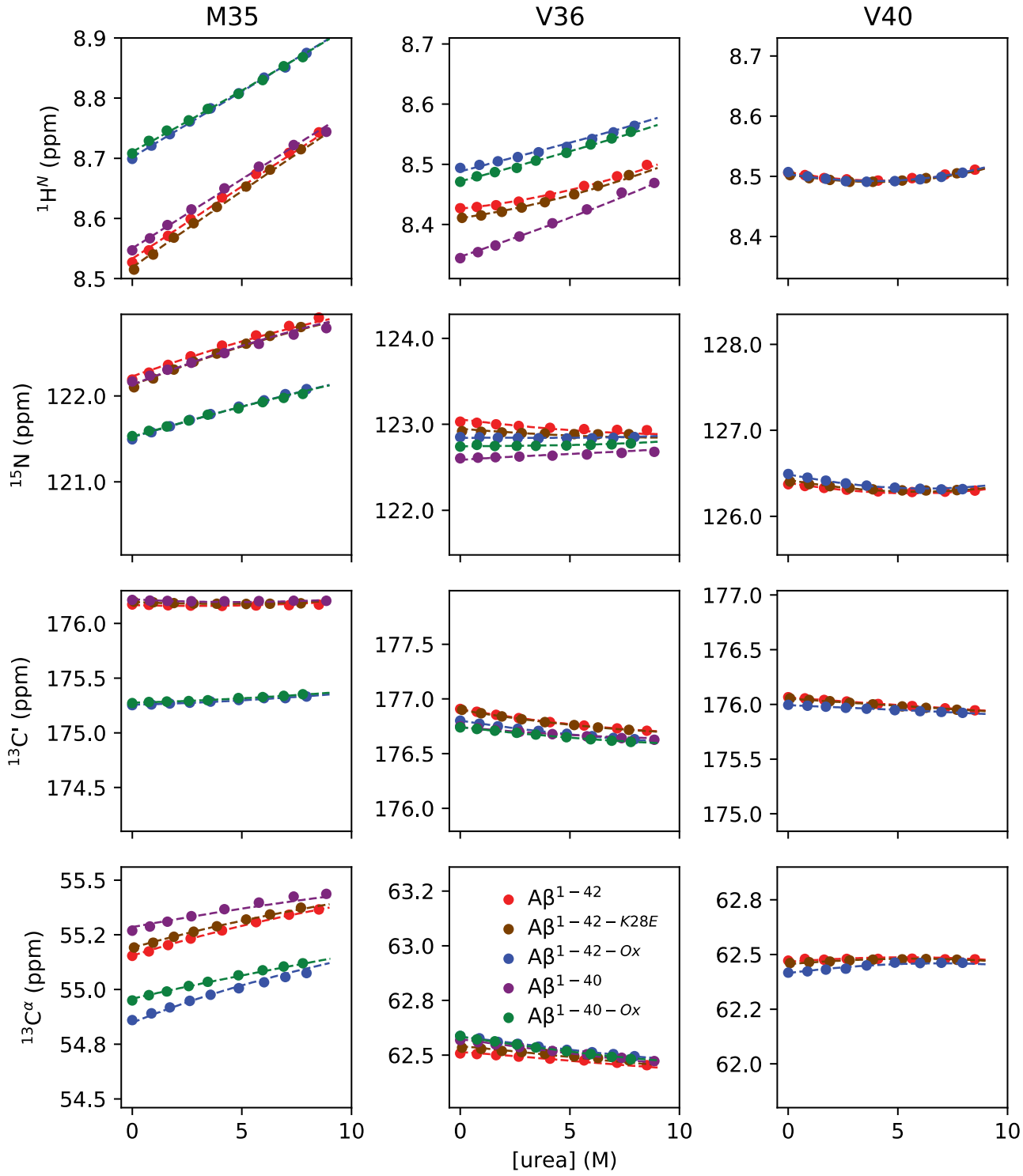
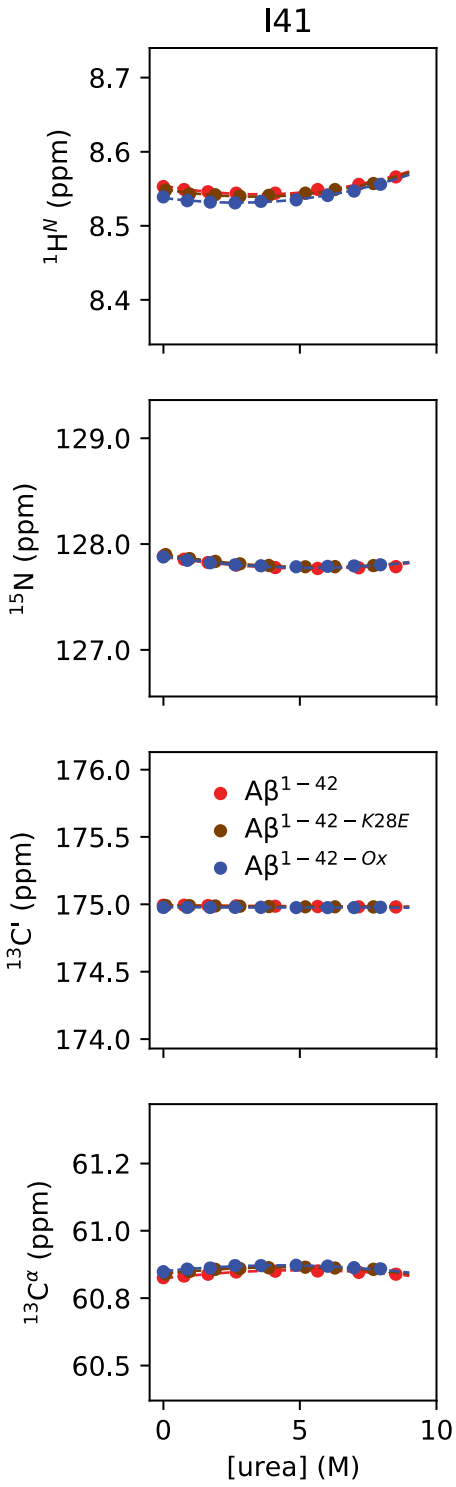


Figure S4 -CONTINUED-



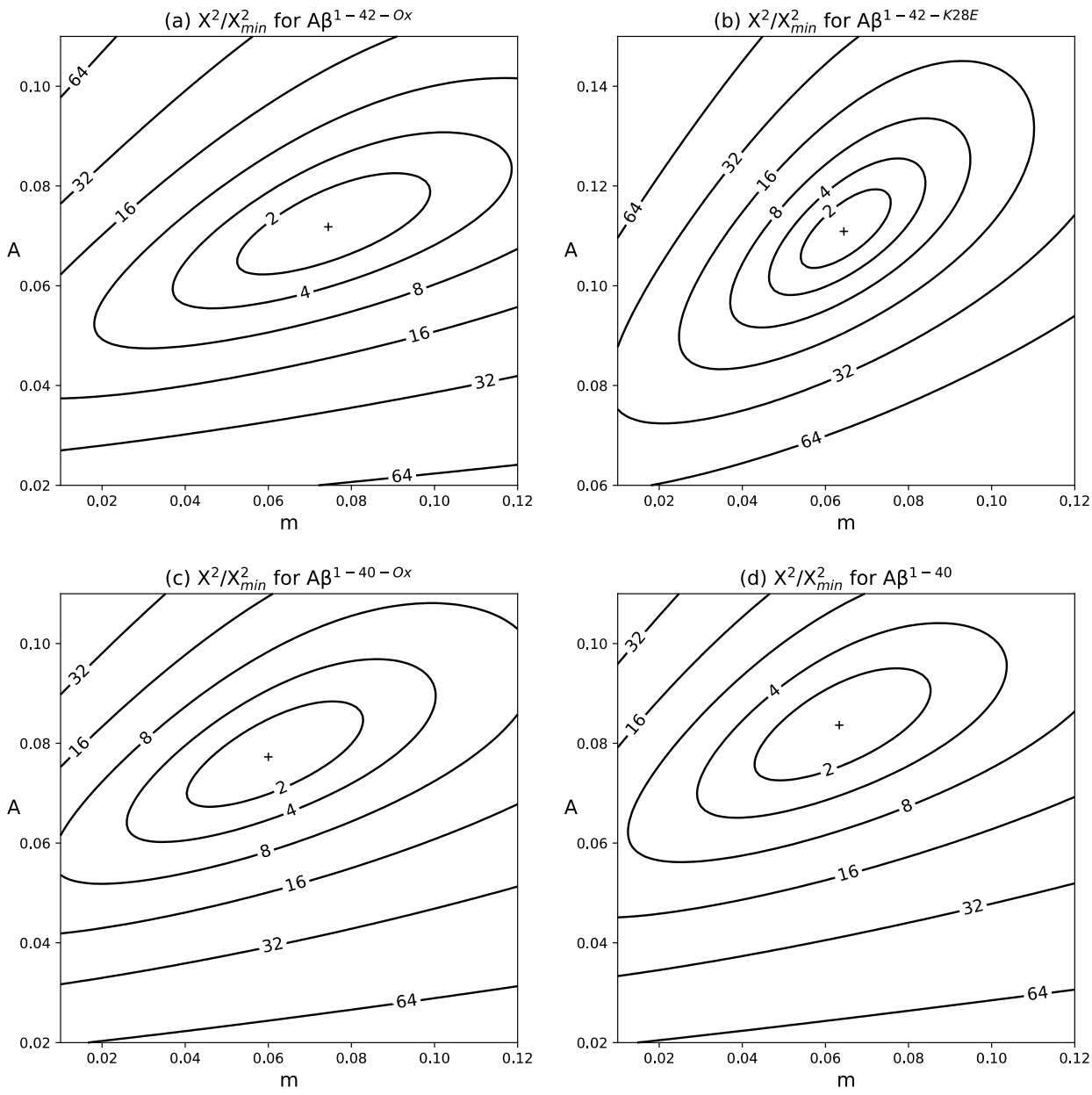


Figure S5. Contour plots of $\chi^2/\chi^2_{\text{min}}$, obtained for (a) $A\beta^{1\text{-}42\text{-}Ox}$, (b) $A\beta^{1\text{-}42\text{-}K28E}$, (c) $A\beta^{1\text{-}40\text{-}Ox}$, (d) $A\beta^{1\text{-}40}$ from a grid search of m and A, with 100 steps in each dimension, followed by best-fitting of the δ_u and δ_f values. The '+' markers correspond to the global minima. Plots are analogous to the one shown for $A\beta^{1\text{-}42}$ in Figure 4, main text.

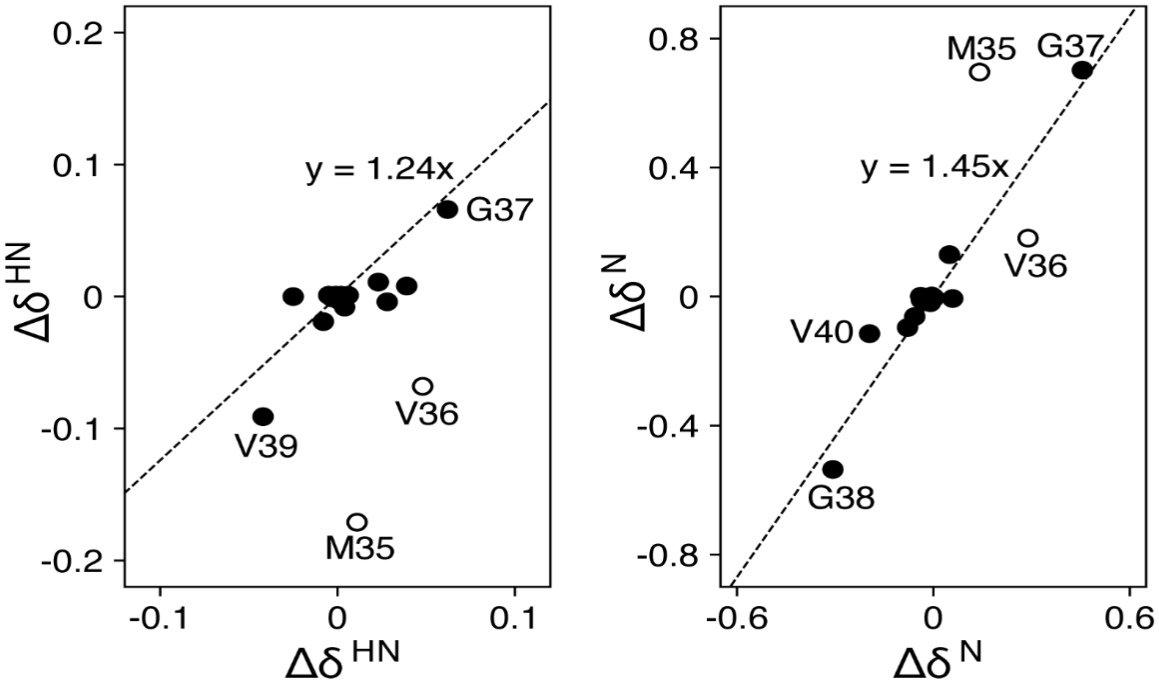


Figure S6. Plots of chemical shift differences between $A\beta^{1-42}$ and $A\beta^{1-42\text{-}Ox}$ (y-axis) versus the chemical shift difference between $A\beta^{1-42\text{-}A42C\text{-}MTSL}$ and $A\beta^{1-42}$. The $A\beta^{1-42}$ – $A\beta^{1-42\text{-}Ox}$ chemical shift differences for M35 and V36 are dominated by the chemical effect of oxidation and not included in the fit. $A\beta^{1-42}$ and $A\beta^{1-42\text{-}Ox}$ The chemical shift difference between $A\beta^{1-42}$ and $A\beta^{1-42\text{-}Ox}$ is attributed to a *ca* 35% decrease in β-sheet population. This fractional change is *ca* 1.24-1.45, or ~1.35-fold larger than the difference in chemical shifts between $A\beta^{1-42\text{-}A42C\text{-}MTSL}$ and $A\beta^{1-42}$, indicating an approximate 35/1.35 ≈ 25% increase in β-sheet population of $A\beta^{1-42\text{-}A42C\text{-}MTSL}$ over $A\beta^{1-42}$.

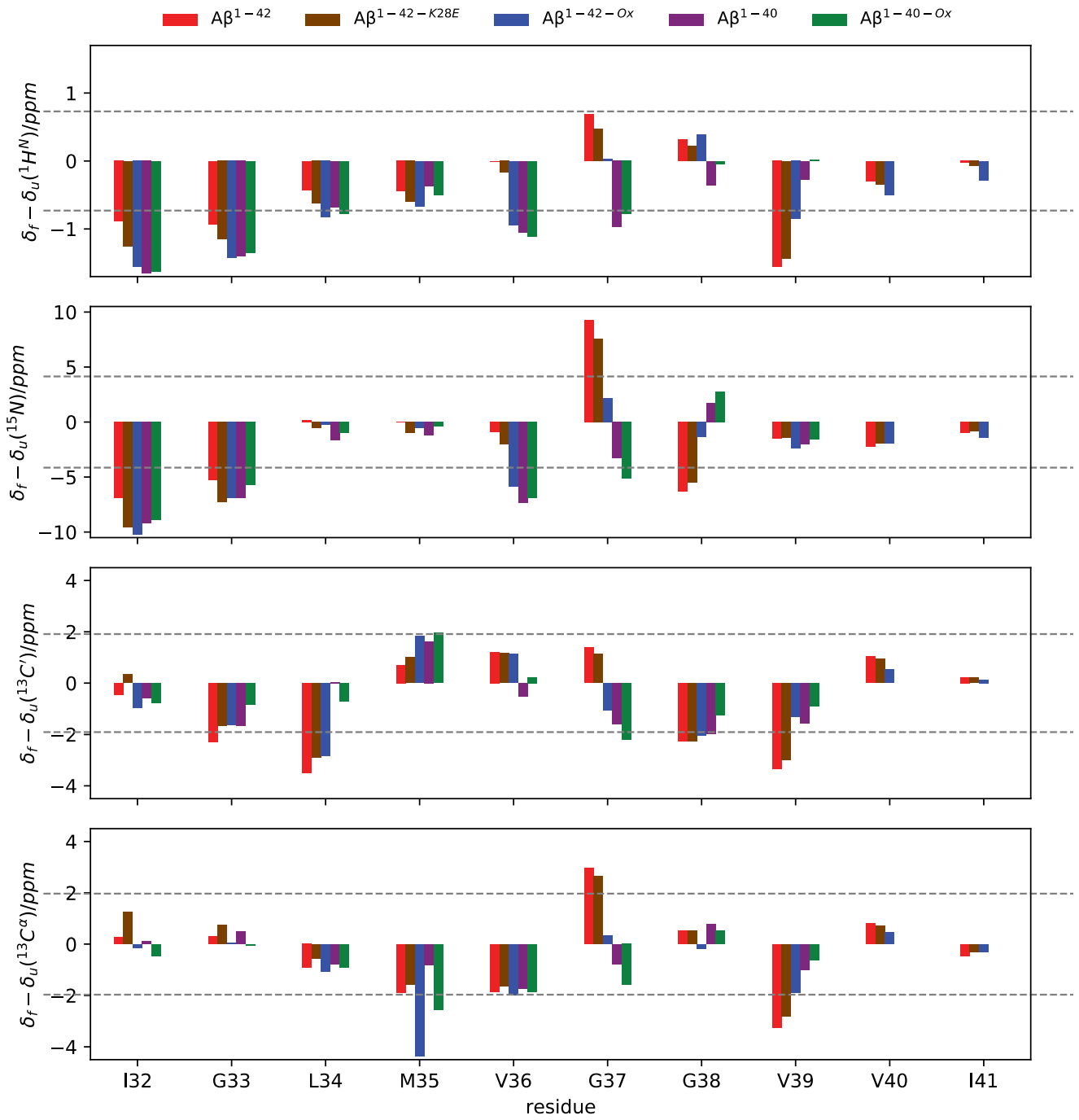


Figure S7. Bar plots of the fitted $\delta_f - \delta_u$ values. The horizontal gray dashed lines represent the rms values for each nucleus obtained from the SPARTA+ database.

Tables

Table S1. Experimental chemical shifts of short reference peptides.

Table S1-A. QIIGQ

urea (M)	0.000	2.873	5.548	8.302
Q1				
$\delta(^{1}H^{N})$	8.415	8.403	8.395	8.389
$\delta(^{15}N)$	126.366	126.329	126.291	126.250
$\delta(^{13}C')$	176.298	176.336	176.357	176.323
$\delta(^{13}C^{\alpha})$	55.962	56.026	56.073	56.117
I2				
$\delta(^{1}H^{N})$	8.473	8.491	8.512	8.542
$\delta(^{15}N)$	123.999	123.946	123.931	123.921
$\delta(^{13}C')$	176.448	176.395	176.367	176.398
$\delta(^{13}C^{\alpha})$	60.922	60.986	61.023	61.051
I3				
$\delta(^{1}H^{N})$	8.522	8.526	8.542	8.567
$\delta(^{15}N)$	127.326	127.301	127.308	127.342
$\delta(^{13}C')$	176.922	176.883	176.854	176.829
$\delta(^{13}C^{\alpha})$	61.259	61.227	61.193	61.161
G4				
$\delta(^{1}H^{N})$	8.724	8.702	8.695	8.691
$\delta(^{15}N)$	114.265	114.218	114.199	114.190
$\delta(^{13}C')$	174.128	174.072	174.027	173.983
$\delta(^{13}C^{\alpha})$	45.262	45.250	45.239	45.233
Q5				
$\delta(^{1}H^{N})$	8.401	8.411	8.421	8.431
$\delta(^{15}N)$	120.792	120.815	120.840	120.872
$\delta(^{13}C')$	178.811	178.789	178.773	178.757
$\delta(^{13}C^{\alpha})$	55.555	55.654	55.725	55.785

Table S1-B. QIGLQ

urea (M)	0.000	2.639	5.198	7.807
Q1				
$\delta(^1H^N)$	8.456	8.441	8.429	8.421
$\delta(^{15}N)$	126.430	126.379	126.340	126.309
$\delta(^{13}C')$	176.569	176.561	176.562	176.569
$\delta(^{13}C^{\alpha})$	55.907	55.961	56.004	56.048
I2				
$\delta(^1H^N)$	8.440	8.453	8.467	8.489
$\delta(^{15}N)$	123.317	123.200	123.111	123.033
$\delta(^{13}C')$	176.968	176.906	176.861	176.822
$\delta(^{13}C^{\alpha})$	61.338	61.357	61.364	61.364
G3				
$\delta(^1H^N)$	8.654	8.635	8.625	8.622
$\delta(^{15}N)$	113.312	113.261	113.232	113.214
$\delta(^{13}C')$	174.314	174.238	174.181	174.127
$\delta(^{13}C^{\alpha})$	45.168	45.160	45.158	45.160
L4				
$\delta(^1H^N)$	8.305	8.306	8.310	8.318
$\delta(^{15}N)$	122.130	122.114	122.110	122.117
$\delta(^{13}C')$	177.806	177.763	177.728	177.695
$\delta(^{13}C^{\alpha})$	55.407	55.388	55.371	55.351
Q5				
$\delta(^1H^N)$	8.540	8.575	8.610	8.650
$\delta(^{15}N)$	121.630	121.696	121.761	121.843
$\delta(^{13}C')$	178.695	178.689	178.689	178.693
$\delta(^{13}C^{\alpha})$	55.684	55.750	55.793	55.828

Table S1-C. QGLMQ

urea (M)	0.000	2.883	5.261	8.009
Q1				
$\delta(^1H^N)$	8.533	8.512	8.489	8.470
$\delta(^{15}N)$	126.114	126.082	126.046	126.007
$\delta(^{13}C')$	177.172	177.135	177.108	177.090
$\delta(^{13}C^{\alpha})$	56.320	56.338	56.343	56.352
G2				
$\delta(^1H^N)$	8.702	8.701	8.692	8.693
$\delta(^{15}N)$	110.437	110.488	110.514	110.535
$\delta(^{13}C')$	174.342	174.248	174.182	174.129
$\delta(^{13}C^{\alpha})$	45.388	45.353	45.327	45.312
L3				
$\delta(^1H^N)$	8.185	8.196	8.198	8.206
$\delta(^{15}N)$	121.496	121.538	121.558	121.591
$\delta(^{13}C')$	177.826	177.790	177.761	177.737
$\delta(^{13}C^{\alpha})$	55.316	55.285	55.256	55.230
M4				
$\delta(^1H^N)$	8.524	8.587	8.632	8.687
$\delta(^{15}N)$	121.103	121.399	121.590	121.774
$\delta(^{13}C')$	176.306	176.316	176.326	176.346
$\delta(^{13}C^{\alpha})$	55.468	55.539	55.577	55.615
Q5				
$\delta(^1H^N)$	8.451	8.514	8.553	8.600
$\delta(^{15}N)$	122.183	122.412	122.553	122.674
$\delta(^{13}C')$	178.614	178.584	178.563	178.552
$\delta(^{13}C^{\alpha})$	55.722	55.776	55.805	55.835

Table S1-D. QLMVQKKK

urea (M)	0.000	2.703	5.229	7.872
Q1				
$\delta(^1H^N)$	8.439	8.421	8.412	8.403
$\delta(^{15}N)$	126.273	126.232	126.202	126.171
$\delta(^{13}C')$	---	---	---	---
$\delta(^{13}C^{\alpha})$	55.961	55.990	56.022	56.051
L2				
$\delta(^1H^N)$	8.491	8.515	8.538	8.563
$\delta(^{15}N)$	124.011	124.109	124.178	124.240
$\delta(^{13}C')$	177.406	177.387	177.377	177.367
$\delta(^{13}C^{\alpha})$	55.207	55.198	55.194	55.188
M3				
$\delta(^1H^N)$	8.538	8.596	8.650	8.708
$\delta(^{15}N)$	122.403	122.658	122.852	123.036
$\delta(^{13}C')$	176.135	176.144	176.166	176.193
$\delta(^{13}C^{\alpha})$	55.278	55.312	55.342	55.371
V4				
$\delta(^1H^N)$	8.279	8.330	8.375	8.424
$\delta(^{15}N)$	122.918	122.954	122.983	123.026
$\delta(^{13}C')$	176.066	176.086	176.109	176.132
$\delta(^{13}C^{\alpha})$	62.388	62.374	62.356	62.356
Q5				
$\delta(^1H^N)$	8.629	8.645	8.665	8.689
$\delta(^{15}N)$	125.354	125.413	125.452	125.492
$\delta(^{13}C')$	---	---	---	---
$\delta(^{13}C^{\alpha})$	55.564	55.614	55.651	55.685
K6				
$\delta(^1H^N)$	8.555	8.595	8.627	8.657
$\delta(^{15}N)$	124.429	124.565	124.654	124.708
$\delta(^{13}C')$	---	---	---	---
$\delta(^{13}C^{\alpha})$	---	---	---	---
K7				
$\delta(^1H^N)$	8.549	8.591	8.630	8.670
$\delta(^{15}N)$	124.636	124.792	124.902	124.977
$\delta(^{13}C')$	---	---	---	---
$\delta(^{13}C^{\alpha})$	---	---	---	---
K8				
$\delta(^1H^N)$	8.178	8.262	8.327	8.392
$\delta(^{15}N)$	128.896	129.127	129.283	129.410
$\delta(^{13}C')$	181.443	181.533	181.586	181.621
$\delta(^{13}C^{\alpha})$	---	---	---	---

Table S1-E. QMVGQ

urea (M)	0.000	2.752	5.367	7.743
Q1				
$\delta(^1H^N)$	8.448	8.434	8.425	8.418
$\delta(^{15}N)$	126.097	126.072	126.049	126.034
$\delta(^{13}C')$	176.498	176.532	176.563	176.587
$\delta(^{13}C^{\alpha})$	56.009	56.063	56.104	56.134
M2				
$\delta(^1H^N)$	8.655	8.675	8.697	8.717
$\delta(^{15}N)$	122.427	122.434	122.452	122.469
$\delta(^{13}C')$	176.372	176.328	176.300	176.282
$\delta(^{13}C^{\alpha})$	55.345	55.428	55.489	55.532
V3				
$\delta(^1H^N)$	8.376	8.390	8.412	8.436
$\delta(^{15}N)$	122.733	122.623	122.550	122.506
$\delta(^{13}C')$	176.936	176.877	176.841	176.813
$\delta(^{13}C^{\alpha})$	62.801	62.726	62.669	62.624
G4				
$\delta(^1H^N)$	8.730	8.701	8.686	8.677
$\delta(^{15}N)$	113.505	113.386	113.306	113.260
$\delta(^{13}C')$	174.200	174.134	174.085	174.047
$\delta(^{13}C^{\alpha})$	45.302	45.276	45.262	45.252
Q5				
$\delta(^1H^N)$	8.375	8.391	8.405	8.413
$\delta(^{15}N)$	120.564	120.574	120.589	120.599
$\delta(^{13}C')$	178.828	178.804	178.786	178.771
$\delta(^{13}C^{\alpha})$	55.541	55.631	55.698	55.745

Table S1-F. QVGGQ

urea (M)	0.000	2.756	5.378	7.780
Q1				
$\delta(^1H^N)$	8.467	8.452	8.438	8.427
$\delta(^{15}N)$	126.501	126.459	126.415	126.378
$\delta(^{13}C')$	176.718	176.714	176.711	176.712
$\delta(^{13}C^{\alpha})$	55.849	55.929	55.985	56.028
V2				
$\delta(^1H^N)$	8.506	8.502	8.502	8.505
$\delta(^{15}N)$	123.011	122.760	122.579	122.450
$\delta(^{13}C')$	177.034	176.969	176.917	176.876
$\delta(^{13}C^{\alpha})$	62.569	62.558	62.540	62.528
G3				
$\delta(^1H^N)$	8.764	8.727	8.701	8.686
$\delta(^{15}N)$	113.619	113.447	113.325	113.244
$\delta(^{13}C')$	174.908	174.830	174.764	174.712
$\delta(^{13}C^{\alpha})$	45.295	45.270	45.251	45.236
G4				
$\delta(^1H^N)$	8.470	8.457	8.447	8.441
$\delta(^{15}N)$	109.073	109.011	108.956	108.913
$\delta(^{13}C')$	174.377	174.339	174.302	174.271
$\delta(^{13}C^{\alpha})$	45.331	45.320	45.312	45.308
Q5				
$\delta(^1H^N)$	8.455	8.471	8.481	8.487
$\delta(^{15}N)$	120.396	120.432	120.451	120.467
$\delta(^{13}C')$	178.866	178.846	178.825	178.810
$\delta(^{13}C^{\alpha})$	55.654	55.761	55.829	55.881

Table S1-G. QGGVQ

urea (M)	0.000	2.718	5.221	7.823
Q1				
$\delta(^1H^N)$	8.550	8.522	8.499	8.477
$\delta(^{15}N)$	126.188	126.149	126.105	126.054
$\delta(^{13}C')$	177.195	177.154	177.126	177.103
$\delta(^{13}C^{\alpha})$	56.215	56.264	56.294	56.317
G2				
$\delta(^1H^N)$	8.728	8.713	8.704	8.697
$\delta(^{15}N)$	110.559	110.510	110.466	110.435
$\delta(^{13}C')$	174.778	174.725	174.683	174.643
$\delta(^{13}C^{\alpha})$	45.326	45.306	45.294	45.289
G3				
$\delta(^1H^N)$	8.377	8.378	8.377	8.379
$\delta(^{15}N)$	108.948	108.915	108.883	108.852
$\delta(^{13}C')$	174.381	174.346	174.316	174.284
$\delta(^{13}C^{\alpha})$	45.051	45.055	45.060	45.068
V4				
$\delta(^1H^N)$	8.221	8.229	8.236	8.245
$\delta(^{15}N)$	119.969	119.845	119.773	119.729
$\delta(^{13}C')$	176.663	176.616	176.576	176.537
$\delta(^{13}C^{\alpha})$	62.601	62.604	62.603	62.603
Q5				
$\delta(^1H^N)$	8.655	8.647	8.645	8.649
$\delta(^{15}N)$	124.970	124.865	124.799	124.761
$\delta(^{13}C')$	178.669	178.647	178.628	178.612
$\delta(^{13}C^{\alpha})$	55.676	55.747	55.788	55.818

Table S1-H. QGVVQ

urea (M)	0.000	2.996	5.407	8.088
Q1				
$\delta(^1H^N)$	8.522	8.492	8.473	8.455
$\delta(^{15}N)$	126.061	126.001	125.964	125.921
$\delta(^{13}C')$	177.067	177.040	177.029	177.024
$\delta(^{13}C^{\alpha})$	56.169	56.202	56.225	56.245
G2				
$\delta(^1H^N)$	8.680	8.669	8.669	8.671
$\delta(^{15}N)$	110.844	110.794	110.770	110.748
$\delta(^{13}C')$	174.002	173.960	173.934	173.909
$\delta(^{13}C^{\alpha})$	45.228	45.204	45.198	45.196
V3				
$\delta(^1H^N)$	8.087	8.098	8.110	8.125
$\delta(^{15}N)$	120.326	120.185	120.114	120.070
$\delta(^{13}C')$	176.520	176.491	176.472	176.450
$\delta(^{13}C^{\alpha})$	62.483	62.465	62.457	62.484
V4				
$\delta(^1H^N)$	8.482	8.462	8.464	8.474
$\delta(^{15}N)$	125.995	125.759	125.647	125.594
$\delta(^{13}C')$	176.288	176.263	176.247	176.231
$\delta(^{13}C^{\alpha})$	62.440	62.465	62.480	62.526
Q5				
$\delta(^1H^N)$	8.677	8.668	8.669	8.678
$\delta(^{15}N)$	126.001	125.929	125.898	125.883
$\delta(^{13}C')$	178.538	178.510	178.494	178.479
$\delta(^{13}C^{\alpha})$	55.661	55.699	55.721	55.737

Table S1-I. QVVIA

urea (M)	0.000	2.667	5.294	8.017
Q1				
$\delta(^1H^N)$	8.420	8.408	8.399	8.394
$\delta(^{15}N)$	126.436	126.381	126.337	126.295
$\delta(^{13}C')$	176.326	176.367	176.401	176.433
$\delta(^{13}C^{\alpha})$	55.854	55.930	55.986	56.039
V2				
$\delta(^1H^N)$	8.414	8.427	8.443	8.466
$\delta(^{15}N)$	123.490	123.313	123.189	123.101
$\delta(^{13}C')$	176.027	176.000	175.976	175.953
$\delta(^{13}C^{\alpha})$	62.439	62.469	62.479	62.494
V3				
$\delta(^1H^N)$	8.533	8.510	8.506	8.513
$\delta(^{15}N)$	126.952	126.791	126.724	126.708
$\delta(^{13}C')$	175.942	175.929	175.913	175.893
$\delta(^{13}C^{\alpha})$	62.351	62.394	62.408	62.419
I4				
$\delta(^1H^N)$	8.542	8.529	8.532	8.550
$\delta(^{15}N)$	127.966	127.842	127.803	127.809
$\delta(^{13}C')$	175.034	175.036	175.037	175.038
$\delta(^{13}C^{\alpha})$	60.921	60.936	60.930	60.913
A5				
$\delta(^1H^N)$	8.157	8.163	8.175	8.194
$\delta(^{15}N)$	102.917	102.755	102.654	102.584
$\delta(^{13}C')$	182.424	182.451	182.451	182.437
$\delta(^{13}C^{\alpha})$	53.914	53.976	54.024	54.067

Table S1-J. QGLMQ^{Ox}

urea (M)	0.000	2.673	5.127	7.815
Q1				
$\delta(^1H^N)$	8.536	8.511	8.495	8.477
$\delta(^{15}N)$	126.099	126.073	126.048	126.009
$\delta(^{13}C')$	177.133	177.109	177.097	177.081
$\delta(^{13}C^{\alpha})$	56.288	56.305	56.319	56.330
G2				
$\delta(^1H^N)$	8.705	8.700	8.697	8.697
$\delta(^{15}N)$	110.461	110.509	110.533	110.540
$\delta(^{13}C')$	174.337	174.259	174.211	174.166
$\delta(^{13}C^{\alpha})$	45.355	45.324	45.312	45.300
L3				
$\delta(^1H^N)$	8.200	8.204	8.211	8.215
$\delta(^{15}N)$	121.335	121.389	121.417	121.441
$\delta(^{13}C')$	177.823	177.799	177.784	177.766
$\delta(^{13}C^{\alpha})$	55.258	55.230	55.211	55.188
M4				
$\delta(^1H^N)$	8.702	8.742	8.788	8.827
$\delta(^{15}N)$	120.462	120.719	120.890	121.063
$\delta(^{13}C')$	175.278	175.323	175.364	175.404
$\delta(^{13}C^{\alpha})$	55.239	55.298	55.345	55.381
Q5				
$\delta(^1H^N)$	8.593	8.635	8.672	8.706
$\delta(^{15}N)$	122.511	122.773	122.919	123.052
$\delta(^{13}C')$	178.584	178.546	178.527	178.507
$\delta(^{13}C^{\alpha})$	55.759	55.813	---	---

Table S1-K. QLMVQKKK^{Ox}

urea (M)	0.000	2.744	5.203	7.829
Q1				
$\delta(^1H^N)$	8.445	8.430	8.419	8.409
$\delta(^{15}N)$	126.220	126.181	126.151	126.122
$\delta(^{13}C')$	176.419	176.481	176.532	176.569
$\delta(^{13}C^{\alpha})$	55.895	55.938	55.980	56.016
L2				
$\delta(^1H^N)$	8.504	8.526	8.546	8.569
$\delta(^{15}N)$	123.974	124.042	124.090	124.131
$\delta(^{13}C')$	177.498	177.502	177.504	177.500
$\delta(^{13}C^{\alpha})$	55.236	55.278	55.272	55.267
M3				
$\delta(^1H^N)$	8.699	8.747	8.794	8.845
$\delta(^{15}N)$	121.553	121.758	121.913	122.083
$\delta(^{13}C')$	175.203	175.257	175.308	175.360
$\delta(^{13}C^{\alpha})$	55.009	55.018	55.049	55.066
V4				
$\delta(^1H^N)$	8.417	8.456	8.489	8.526
$\delta(^{15}N)$	122.985	123.005	123.021	123.064
$\delta(^{13}C')$	176.097	176.107	176.118	176.128
$\delta(^{13}C^{\alpha})$	62.459	62.444	62.427	62.417
Q5				
$\delta(^1H^N)$	8.670	8.683	8.696	8.717
$\delta(^{15}N)$	125.352	125.373	125.379	125.404
$\delta(^{13}C')$	175.752	175.849	175.907	175.944
$\delta(^{13}C^{\alpha})$	55.553	55.604	55.655	55.687
K6				
$\delta(^1H^N)$	8.578	8.612	8.637	8.664
$\delta(^{15}N)$	124.559	124.668	124.730	124.767
$\delta(^{13}C')$	176.465	176.507	176.540	176.573
$\delta(^{13}C^{\alpha})$	56.329	56.398	56.444	56.480
K7				
$\delta(^1H^N)$	8.557	8.594	8.631	8.669
$\delta(^{15}N)$	124.671	124.805	124.895	124.977
$\delta(^{13}C')$	175.809	175.863	175.918	175.987
$\delta(^{13}C^{\alpha})$	56.518	56.608	56.665	56.709
K8				
$\delta(^1H^N)$	8.180	8.260	8.325	8.388
$\delta(^{15}N)$	128.892	129.119	129.271	129.397
$\delta(^{13}C')$	---	---	---	---
$\delta(^{13}C^{\alpha})$	57.969	58.138	58.255	58.355

Table S1-L. QMVGQ^{Ox}

urea (M)	0.000	2.602	5.159	7.783
Q1				
$\delta(^1H^N)$	8.466	8.449	8.440	8.431
$\delta(^{15}N)$	125.980	125.962	125.944	125.928
$\delta(^{13}C')$	176.537	176.572	176.602	176.631
$\delta(^{13}C^{\alpha})$	56.016	56.067	56.106	56.149
M2				
$\delta(^1H^N)$	8.794	8.806	8.824	8.843
$\delta(^{15}N)$	121.592	121.630	121.672	121.715
$\delta(^{13}C')$	175.382	175.374	175.375	175.379
$\delta(^{13}C^{\alpha})$	55.053	55.133	55.192	55.242
V3				
$\delta(^1H^N)$	8.510	8.515	8.530	8.545
$\delta(^{15}N)$	122.876	122.761	122.678	122.631
$\delta(^{13}C')$	176.887	176.829	176.793	176.757
$\delta(^{13}C^{\alpha})$	62.807	62.732	62.678	62.628
G4				
$\delta(^1H^N)$	8.740	8.710	8.693	8.685
$\delta(^{15}N)$	113.428	113.319	113.214	113.141
$\delta(^{13}C')$	174.151	174.091	174.050	174.014
$\delta(^{13}C^{\alpha})$	45.228	45.208	45.198	45.194
Q5				
$\delta(^1H^N)$	8.406	8.418	8.429	8.439
$\delta(^{15}N)$	120.574	120.594	120.610	120.623
$\delta(^{13}C')$	178.860	178.836	178.819	178.803
$\delta(^{13}C^{\alpha})$	55.581	55.666	55.729	55.783

Table S2. Experimental chemical shifts of Aβ peptides. ^{1}H chemical shifts are directly referenced vs. internal DSS and indirectly vs. DSS for ^{13}C and ^{15}N. The first row shows the urea concentration.

Table S2-A. Aβ$^{1-40}$

urea (M)	0.000	0.806	1.606	2.697	4.204	5.776	7.362	8.851
δ($^{1}H^{N}$) [I32]	8.387	8.397	8.409	8.425	8.447	8.470	8.497	8.512
δ(^{15}N) [I32]	126.475	126.542	126.608	126.682	126.778	126.867	126.957	127.012
δ($^{13}C'$) [I32]	176.701	176.687	176.676	176.665	176.653	176.643	176.636	176.626
δ($^{13}C^{\alpha}$) [I32]	61.212	61.196	61.182	61.168	61.149	61.129	61.111	61.090
δ($^{1}H^{N}$) [G33]	8.570	8.573	8.575	8.580	8.585	8.591	8.600	8.603
δ(^{15}N) [G33]	113.268	113.313	113.352	113.395	113.445	113.486	113.527	113.550
δ($^{13}C'$) [G33]	173.757	173.740	173.724	173.706	173.684	173.661	173.639	173.620
δ($^{13}C^{\alpha}$) [G33]	45.146	45.134	45.127	45.118	45.111	45.104	45.102	45.094
δ($^{1}H^{N}$) [L34]	8.150	8.156	8.163	8.170	8.179	8.188	8.198	8.202
δ(^{15}N) [L34]	121.813	121.830	121.844	121.863	121.888	121.914	121.940	121.956
δ($^{13}C'$) [L34]	177.375	177.374	177.374	177.373	177.369	177.364	177.356	177.344
δ($^{13}C^{\alpha}$) [L34]	55.135	55.132	55.129	55.125	55.119	55.111	55.103	55.092
δ($^{1}H^{N}$) [M35]	8.547	8.567	8.589	8.615	8.650	8.686	8.722	8.744
δ(^{15}N) [M35]	122.168	122.235	122.305	122.386	122.498	122.606	122.714	122.789
δ($^{13}C'$) [M35]	176.215	176.209	176.206	176.203	176.203	176.204	176.208	176.207
δ($^{13}C^{\alpha}$) [M35]	55.269	55.288	55.310	55.335	55.367	55.397	55.425	55.437
δ($^{1}H^{N}$) [V36]	8.344	8.354	8.365	8.380	8.402	8.425	8.453	8.469
δ(^{15}N) [V36]	122.605	122.612	122.617	122.624	122.635	122.649	122.667	122.680
δ($^{13}C'$) [V36]	176.750	176.733	176.717	176.699	176.678	176.658	176.642	176.627
δ($^{13}C^{\alpha}$) [V36]	62.569	62.559	62.549	62.537	62.519	62.504	62.488	62.473
δ($^{1}H^{N}$) [G37]	8.701	8.694	8.688	8.681	8.673	8.667	8.664	8.658
δ(^{15}N) [G37]	113.343	113.312	113.277	113.237	113.188	113.141	113.101	113.073
δ($^{13}C'$) [G37]	174.514	174.499	174.483	174.465	174.439	174.414	174.389	174.367
δ($^{13}C^{\alpha}$) [G37]	45.205	45.196	45.188	45.180	45.171	45.162	45.155	45.144
δ($^{1}H^{N}$) [G38]	8.352	8.353	8.354	8.356	8.358	8.359	8.362	8.360
δ(^{15}N) [G38]	108.843	108.830	108.816	108.799	108.776	108.751	108.727	108.705
δ($^{13}C'$) [G38]	173.751	173.752	173.753	173.753	173.748	173.741	173.731	173.716
δ($^{13}C^{\alpha}$) [G38]	45.050	45.046	45.045	45.043	45.042	45.041	45.042	45.038
δ($^{1}H^{N}$) [V39]	8.176	8.180	8.186	8.192	8.200	8.208	8.219	8.221
δ(^{15}N) [V39]	120.064	120.031	120.003	119.971	119.941	119.918	119.909	119.900
δ($^{13}C'$) [V39]	175.616	175.618	175.621	175.622	175.623	175.620	175.619	175.611
δ($^{13}C^{\alpha}$) [V39]	62.480	62.486	62.492	62.500	62.509	62.514	62.518	62.514
δ($^{1}H^{N}$) [V40]	7.922	7.928	7.934	7.944	7.957	7.973	7.993	8.005
δ(^{15}N) [V40]	128.558	128.542	128.526	128.511	128.502	128.500	128.513	128.522
δ($^{13}C'$) [V40]	---	---	---	---	---	---	---	---
δ($^{13}C^{\alpha}$) [V40]	---	---	---	---	---	---	---	---

Table S2-B. $A\beta^{1\text{-}40\text{-}Ox}$

urea (M)	0.000	0.759	1.577	2.576	3.447	4.843	5.948	6.907	7.780
$\delta(^1H^N)$ [I32]	8.398	8.407	8.417	8.428	8.440	8.459	8.477	8.492	8.505
$\delta(^{15}N)$ [I32]	126.558	126.613	126.659	126.713	126.761	126.832	126.886	126.934	126.976
$\delta(^{13}C')$ [I32]	176.685	176.676	176.667	176.659	176.653	176.644	176.641	176.638	176.636
$\delta(^{13}C^\alpha)$ [I32]	61.174	61.159	61.146	61.138	61.128	61.115	61.107	61.099	61.087
$\delta(^1H^N)$ [G33]	8.579	8.581	8.583	8.586	8.589	8.593	8.597	8.603	8.608
$\delta(^{15}N)$ [G33]	113.386	113.421	113.444	113.475	113.496	113.522	113.541	113.564	113.581
$\delta(^{13}C')$ [G33]	173.790	173.779	173.772	173.758	173.748	173.734	173.722	173.713	173.704
$\delta(^{13}C^\alpha)$ [G33]	45.103	45.093	45.090	45.089	45.087	45.086	45.087	45.089	45.093
$\delta(^1H^N)$ [L34]	8.172	8.179	8.184	8.190	8.195	8.201	8.207	8.213	8.218
$\delta(^{15}N)$ [L34]	121.763	121.781	121.799	121.816	121.833	121.851	121.867	121.883	121.897
$\delta(^{13}C')$ [L34]	177.462	177.465	177.470	177.465	177.465	177.461	177.454	177.456	177.451
$\delta(^{13}C^\alpha)$ [L34]	55.141	55.147	55.139	55.140	55.135	55.124	55.120	55.121	55.116
$\delta(^1H^N)$ [M35]	8.708	8.729	8.746	8.763	8.782	8.807	8.830	8.853	8.868
$\delta(^{15}N)$ [M35]	121.533	121.594	121.645	121.715	121.782	121.855	121.928	121.977	122.023
$\delta(^{13}C')$ [M35]	175.272	175.282	175.286	175.291	175.298	175.318	175.327	175.338	175.353
$\delta(^{13}C^\alpha)$ [M35]	54.950	54.974	54.991	55.016	55.035	55.065	55.088	55.105	55.120
$\delta(^1H^N)$ [V36]	8.471	8.480	8.487	8.494	8.506	8.519	8.533	8.543	8.554
$\delta(^{15}N)$ [V36]	122.741	122.761	122.748	122.749	122.750	122.753	122.761	122.767	122.777
$\delta(^{13}C')$ [V36]	176.740	176.726	176.710	176.690	176.674	176.650	176.631	176.618	176.607
$\delta(^{13}C^\alpha)$ [V36]	62.588	62.572	62.563	62.549	62.535	62.518	62.505	62.492	62.482
$\delta(^1H^N)$ [G37]	8.717	8.709	8.704	8.695	8.689	8.682	8.678	8.675	8.673
$\delta(^{15}N)$ [G37]	113.292	113.243	113.202	113.155	113.115	113.061	113.019	112.985	112.961
$\delta(^{13}C')$ [G37]	174.482	174.470	174.457	174.439	174.425	174.404	174.386	174.373	174.361
$\delta(^{13}C^\alpha)$ [G37]	45.157	45.152	45.149	45.141	45.133	45.129	45.123	45.120	45.117
$\delta(^1H^N)$ [G38]	8.372	8.372	8.373	8.373	8.374	8.374	8.376	8.377	8.379
$\delta(^{15}N)$ [G38]	108.909	108.891	108.875	108.853	108.837	108.807	108.787	108.770	108.757
$\delta(^{13}C')$ [G38]	173.798	173.802	173.800	173.799	173.797	173.789	173.783	173.777	173.769
$\delta(^{13}C^\alpha)$ [G38]	45.032	45.029	45.028	45.027	45.025	45.025	45.025	45.027	45.028
$\delta(^1H^N)$ [V39]	8.193	8.198	8.202	8.207	8.212	8.218	8.225	8.230	8.236
$\delta(^{15}N)$ [V39]	120.099	120.063	120.036	120.006	119.985	119.955	119.940	119.931	119.928
$\delta(^{13}C')$ [V39]	175.663	175.666	175.666	175.664	175.663	175.659	175.656	175.653	175.650
$\delta(^{13}C^\alpha)$ [V39]	62.504	62.510	62.515	62.519	62.524	62.530	62.533	62.535	62.536
$\delta(^1H^N)$ [V40]	7.925	7.934	7.936	7.944	7.952	7.965	7.978	7.989	8.000
$\delta(^{15}N)$ [V40]	128.577	128.558	128.544	128.529	128.519	128.511	128.510	128.514	128.522
$\delta(^{13}C')$ [V40]	---	---	---	---	---	---	---	---	---
$\delta(^{13}C^\alpha)$ [V40]	---	---	---	---	---	---	---	---	---

Table S2-C. Aβ$^{1-42}$

urea (M)	0.000	0.759	1.634	2.667	4.094	5.648	7.153	8.512
δ($^{1}H^{N}$) [I32]	8.420	8.427	8.437	8.450	8.469	8.490	8.513	8.535
δ(^{15}N) [I32]	126.477	126.535	126.601	126.675	126.764	126.857	126.939	127.013
δ($^{13}C'$) [I32]	176.699	176.687	176.675	176.665	176.651	176.643	176.635	176.629
δ($^{13}C^{\alpha}$) [I32]	61.230	61.219	61.201	61.183	61.162	61.139	61.119	61.102
δ($^{1}H^{N}$) [G33]	8.579	8.582	8.585	8.589	8.594	8.601	8.608	8.616
δ(^{15}N) [G33]	113.264	113.303	113.344	113.384	113.429	113.471	113.508	113.543
δ($^{13}C'$) [G33]	173.657	173.649	173.638	173.627	173.611	173.597	173.582	173.566
δ($^{13}C^{\alpha}$) [G33]	45.136	45.128	45.121	45.114	45.109	45.105	45.105	45.102
δ($^{1}H^{N}$) [L34]	8.155	8.161	8.168	8.175	8.184	8.195	8.205	8.214
δ(^{15}N) [L34]	121.940	121.953	121.966	121.980	121.996	122.015	122.035	122.050
δ($^{13}C'$) [L34]	177.043	177.061	177.079	177.098	177.119	177.138	177.152	177.162
δ($^{13}C^{\alpha}$) [L34]	55.106	55.106	55.102	55.099	55.093	55.091	55.083	55.076
δ($^{1}H^{N}$) [M35]	8.527	8.547	8.571	8.599	8.635	8.674	8.709	8.743
δ(^{15}N) [M35]	122.191	122.271	122.361	122.461	122.586	122.704	122.814	122.911
δ($^{13}C'$) [M35]	176.174	176.170	176.166	176.163	176.161	176.164	176.167	176.172
δ($^{13}C^{\alpha}$) [M35]	55.154	55.174	55.203	55.233	55.270	55.308	55.342	55.366
δ($^{1}H^{N}$) [V36]	8.427	8.429	8.432	8.438	8.448	8.464	8.480	8.499
δ(^{15}N) [V36]	123.030	123.017	123.000	122.981	122.959	122.944	122.935	122.932
δ($^{13}C'$) [V36]	176.908	176.883	176.855	176.825	176.788	176.757	176.731	176.709
δ($^{13}C^{\alpha}$) [V36]	62.508	62.505	62.500	62.493	62.484	62.476	62.465	62.454
δ($^{1}H^{N}$) [G37]	8.844	8.827	8.809	8.790	8.768	8.751	8.737	8.726
δ(^{15}N) [G37]	114.483	114.383	114.268	114.146	114.000	113.870	113.758	113.663
δ($^{13}C'$) [G37]	174.766	174.737	174.702	174.664	174.617	174.574	174.534	174.500
δ($^{13}C^{\alpha}$) [G37]	45.539	45.513	45.484	45.454	45.419	45.391	45.364	45.338
δ($^{1}H^{N}$) [G38]	8.410	8.407	8.404	8.400	8.395	8.393	8.391	8.390
δ(^{15}N) [G38]	108.088	108.130	108.173	108.217	108.263	108.300	108.329	108.349
δ($^{13}C'$) [G38]	173.662	173.672	173.680	173.690	173.699	173.706	173.708	173.709
δ($^{13}C^{\alpha}$) [G38]	45.046	45.045	45.041	45.039	45.036	45.036	45.037	45.036
δ($^{1}H^{N}$) [V39]	8.013	8.027	8.042	8.060	8.081	8.105	8.126	8.145
δ(^{15}N) [V39]	119.978	119.958	119.930	119.906	119.876	119.856	119.841	119.833
δ($^{13}C'$) [V39]	175.727	175.750	175.773	175.796	175.821	175.841	175.857	175.868
δ($^{13}C^{\alpha}$) [V39]	61.959	61.984	62.012	62.043	62.078	62.110	62.135	62.156
δ($^{1}H^{N}$) [V40]	8.506	8.502	8.497	8.495	8.493	8.497	8.503	8.511
δ(^{15}N) [V40]	126.373	126.353	126.330	126.309	126.289	126.282	126.286	126.299
δ($^{13}C'$) [V40]	176.066	176.055	176.041	176.026	176.004	175.985	175.964	175.946
δ($^{13}C^{\alpha}$) [V40]	62.472	62.480	62.476	62.480	62.480	62.481	62.478	62.478
δ($^{1}H^{N}$) [I41]	8.553	8.549	8.546	8.544	8.544	8.549	8.556	8.566
δ(^{15}N) [I41]	127.886	127.856	127.825	127.800	127.777	127.769	127.775	127.786
δ($^{13}C'$) [I41]	174.994	174.993	174.991	174.989	174.986	174.984	174.982	174.981
δ($^{13}C^{\alpha}$) [I41]	60.826	60.832	60.839	60.847	60.850	60.851	60.846	60.839

Table S2-D. $A\beta^{1\text{-}42\text{-}Ox}$

urea (M)	0.000	0.875	1.716	2.624	3.573	4.861	6.013	6.983	7.949
δ($^{1}H^{N}$) [I32]	8.411	8.421	8.431	8.443	8.458	8.473	8.490	8.507	8.524
δ(^{15}N) [I32]	126.552	126.608	126.660	126.719	126.757	126.829	126.892	126.938	126.990
δ($^{13}C'$) [I32]	176.684	176.670	176.660	176.651	176.648	176.638	176.635	176.631	176.630
δ($^{13}C^{\alpha}$) [I32]	61.190	61.173	61.163	61.154	61.149	61.132	61.122	61.113	61.101
δ($^{1}H^{N}$) [G33]	8.584	8.585	8.588	8.591	8.593	8.598	8.604	8.609	8.614
δ(^{15}N) [G33]	113.369	113.402	113.433	113.461	113.469	113.502	113.524	113.551	113.568
δ($^{13}C'$) [G33]	173.753	173.742	173.732	173.724	173.714	173.702	173.694	173.685	173.677
δ($^{13}C^{\alpha}$) [G33]	45.104	45.097	45.095	45.094	45.090	45.091	45.092	45.095	45.095
δ($^{1}H^{N}$) [L34]	8.173	8.180	8.186	8.193	8.198	8.204	8.212	8.217	8.225
δ(^{15}N) [L34]	121.808	121.828	121.846	121.861	121.874	121.893	121.911	121.922	121.937
δ($^{13}C'$) [L34]	177.343	177.354	177.359	177.366	177.374	177.376	177.384	177.380	177.384
δ($^{13}C^{\alpha}$) [L34]	55.139	55.133	55.137	55.142	55.134	55.131	55.123	55.114	55.109
δ($^{1}H^{N}$) [M35]	8.699	8.721	8.740	8.761	8.783	8.808	8.834	8.851	8.875
δ(^{15}N) [M35]	121.496	121.577	121.647	121.720	121.789	121.876	121.949	122.020	122.079
δ($^{13}C'$) [M35]	175.253	175.259	175.268	175.275	175.286	175.300	175.318	175.317	175.332
δ($^{13}C^{\alpha}$) [M35]	54.860	54.891	54.918	54.948	54.976	55.006	55.033	55.057	55.075
δ($^{1}H^{N}$) [V36]	8.494	8.499	8.505	8.512	8.520	8.529	8.542	8.553	8.564
δ(^{15}N) [V36]	122.852	122.850	122.844	122.841	122.837	122.836	122.837	122.843	122.852
δ($^{13}C'$) [V36]	176.801	176.773	176.750	176.727	176.708	176.681	176.660	176.644	176.632
δ($^{13}C^{\alpha}$) [V36]	62.588	62.577	62.560	62.552	62.539	62.524	62.513	62.505	62.495
δ($^{1}H^{N}$) [G37]	8.778	8.763	8.750	8.737	8.727	8.715	8.708	8.702	8.699
δ(^{15}N) [G37]	113.788	113.695	113.608	113.526	113.455	113.369	113.303	113.256	113.211
δ($^{13}C'$) [G37]	174.575	174.549	174.526	174.504	174.482	174.456	174.434	174.416	174.401
δ($^{13}C^{\alpha}$) [G37]	45.291	45.271	45.256	45.237	45.227	45.214	45.201	45.192	45.182
δ($^{1}H^{N}$) [G38]	8.400	8.397	8.395	8.394	8.393	8.392	8.392	8.392	8.394
δ(^{15}N) [G38]	108.625	108.630	108.633	108.635	108.634	108.628	108.620	108.614	108.609
δ($^{13}C'$) [G38]	173.749	173.756	173.760	173.766	173.771	173.772	173.774	173.774	173.772
δ($^{13}C^{\alpha}$) [G38]	44.995	44.991	44.989	44.989	44.986	44.988	44.987	44.988	44.990
δ($^{1}H^{N}$) [V39]	8.104	8.116	8.127	8.139	8.151	8.165	8.179	8.190	8.202
δ(^{15}N) [V39]	119.988	119.953	119.928	119.901	119.879	119.855	119.839	119.831	119.824
δ($^{13}C'$) [V39]	175.970	175.977	175.983	175.989	175.992	175.992	175.993	175.993	175.992
δ($^{13}C^{\alpha}$) [V39]	62.153	62.171	62.187	62.201	62.219	62.228	62.238	62.243	62.250
δ($^{1}H^{N}$) [V40]	8.507	8.500	8.496	8.492	8.491	8.492	8.495	8.499	8.506
δ(^{15}N) [V40]	126.492	126.450	126.415	126.383	126.357	126.333	126.320	126.313	126.316
δ($^{13}C'$) [V40]	175.996	175.988	175.979	175.969	175.961	175.948	175.938	175.931	175.923
δ($^{13}C^{\alpha}$) [V40]	62.417	62.423	62.431	62.435	62.450	62.463	62.461	62.462	62.462
δ($^{1}H^{N}$) [I41]	8.539	8.534	8.532	8.531	8.533	8.535	8.541	8.547	8.556
δ(^{15}N) [I41]	127.878	127.846	127.823	127.804	127.794	127.785	127.789	127.793	127.804
δ($^{13}C'$) [I41]	174.977	174.977	174.977	174.978	174.978	174.976	174.976	174.976	174.978
δ($^{13}C^{\alpha}$) [I41]	60.848	60.858	60.862	60.871	60.871	60.872	60.869	60.863	60.859
δ($^{1}H^{N}$) [A42]	8.150	8.153	8.155	8.159	8.164	8.170	8.179	8.185	8.195
δ(^{15}N) [A42]	112.929	112.881	112.842	112.803	112.770	112.730	112.700	112.679	112.661
δ($^{13}C'$) [A42]	---	---	---	---	---	---	---	---	---
δ($^{13}C^{\alpha}$) [A42]	---	---	---	---	---	---	---	---	---

Table S2-E. $A\beta^{1\text{-}42\text{-}K28E}$

urea (M)	0.083	0.954	1.899	2.801	3.859	5.197	6.282	7.693
$\delta(^1H^N)$ [I32]	8.390	8.401	8.415	8.427	8.441	8.461	8.478	8.501
$\delta(^{15}N)$ [I32]	126.274	126.352	126.430	126.498	126.568	126.656	126.723	126.801
$\delta(^{13}C')$ [I32]	176.772	176.753	176.736	176.724	176.710	176.698	176.689	176.680
$\delta(^{13}C^\alpha)$ [I32]	61.316	61.294	61.272	61.255	61.236	61.215	61.198	61.173
$\delta(^1H^N)$ [G33]	8.561	8.566	8.571	8.574	8.579	8.586	8.592	8.601
$\delta(^{15}N)$ [G33]	113.099	113.155	113.206	113.246	113.290	113.336	113.374	113.416
$\delta(^{13}C')$ [G33]	173.721	173.705	173.691	173.676	173.663	173.645	173.633	173.616
$\delta(^{13}C^\alpha)$ [G33]	45.173	45.163	45.154	45.148	45.141	45.137	45.132	45.131
$\delta(^1H^N)$ [L34]	8.138	8.147	8.156	8.163	8.170	8.180	8.188	8.199
$\delta(^{15}N)$ [L34]	121.867	121.890	121.909	121.926	121.946	121.967	121.987	122.009
$\delta(^{13}C')$ [L34]	177.113	177.126	177.139	177.150	177.161	177.173	177.182	177.191
$\delta(^{13}C^\alpha)$ [L34]	55.146	55.137	55.134	55.126	55.121	55.114	55.107	55.100
$\delta(^1H^N)$ [M35]	8.515	8.540	8.568	8.592	8.619	8.653	8.681	8.715
$\delta(^{15}N)$ [M35]	122.101	122.203	122.307	122.398	122.493	122.608	122.699	122.802
$\delta(^{13}C')$ [M35]	176.199	176.193	176.186	176.182	176.180	176.178	176.180	176.184
$\delta(^{13}C^\alpha)$ [M35]	55.192	55.214	55.241	55.264	55.289	55.320	55.343	55.374
$\delta(^1H^N)$ [V36]	8.411	8.415	8.421	8.428	8.437	8.450	8.464	8.482
$\delta(^{15}N)$ [V36]	122.920	122.913	122.906	122.898	122.893	122.886	122.884	122.885
$\delta(^{13}C')$ [V36]	176.900	176.869	176.840	176.814	176.788	176.761	176.739	176.717
$\delta(^{13}C^\alpha)$ [V36]	62.534	62.529	62.519	62.514	62.506	62.494	62.487	62.476
$\delta(^1H^N)$ [G37]	8.821	8.802	8.786	8.770	8.756	8.742	8.732	8.722
$\delta(^{15}N)$ [G37]	114.296	114.184	114.078	113.985	113.888	113.780	113.700	113.612
$\delta(^{13}C')$ [G37]	174.739	174.703	174.669	174.637	174.605	174.568	174.538	174.505
$\delta(^{13}C^\alpha)$ [G37]	45.501	45.471	45.444	45.419	45.395	45.369	45.349	45.328
$\delta(^1H^N)$ [G38]	8.401	8.397	8.395	8.392	8.390	8.388	8.387	8.387
$\delta(^{15}N)$ [G38]	108.181	108.226	108.264	108.292	108.322	108.351	108.368	108.388
$\delta(^{13}C')$ [G38]	173.670	173.680	173.690	173.695	173.702	173.708	173.711	173.713
$\delta(^{13}C^\alpha)$ [G38]	45.045	45.042	45.038	45.035	45.035	45.031	45.032	45.031
$\delta(^1H^N)$ [V39]	8.028	8.044	8.060	8.074	8.090	8.109	8.126	8.145
$\delta(^{15}N)$ [V39]	119.984	119.958	119.929	119.908	119.887	119.866	119.853	119.844
$\delta(^{13}C')$ [V39]	175.767	175.792	175.813	175.829	175.846	175.862	175.873	175.884
$\delta(^{13}C^\alpha)$ [V39]	62.004	62.033	62.061	62.083	62.107	62.133	62.154	62.175
$\delta(^1H^N)$ [V40]	8.502	8.497	8.494	8.491	8.491	8.493	8.497	8.505
$\delta(^{15}N)$ [V40]	126.404	126.374	126.350	126.330	126.313	126.301	126.300	126.305
$\delta(^{13}C')$ [V40]	176.055	176.041	176.029	176.015	176.001	175.982	175.969	175.951
$\delta(^{13}C^\alpha)$ [V40]	62.461	62.465	62.468	62.473	62.476	62.478	62.479	62.476
$\delta(^1H^N)$ [I41]	8.548	8.543	8.542	8.540	8.541	8.544	8.549	8.557
$\delta(^{15}N)$ [I41]	127.900	127.863	127.835	127.813	127.797	127.785	127.786	127.796
$\delta(^{13}C')$ [I41]	174.991	174.990	174.988	174.986	174.984	174.982	174.982	174.981
$\delta(^{13}C^\alpha)$ [I41]	60.840	60.849	60.857	60.860	60.863	60.865	60.862	60.857

Table S3. Best-fitted chemical shift values (ppm) for the folded conformer (δ_f) and their difference relative to the fully unfolded state (δ_u).

$A\beta^{1-42}$

Res.	δ_f ($^1H^N$)	δ_f (^{15}N)	δ_f ($^{13}C'$)	δ_f ($^{13}C^\alpha$)	$\delta_f - \delta_u$ ($^1H^N$)	$\delta_f - \delta_u$ (^{15}N)	$\delta_f - \delta_u$ ($^{13}C'$)	$\delta_f - \delta_u$ ($^{13}C^\alpha$)
I32	7.625	120.284	176.277	61.462	-0.891	-6.944	-0.460	0.268
G33	7.749	108.548	171.567	45.409	-0.929	-5.283	-2.309	0.310
L34	7.772	122.151	173.890	54.283	-0.430	0.221	-3.511	-0.917
M35	8.132	122.265	176.805	53.450	-0.447	0.042	0.709	-1.898
V36	8.417	122.210	177.996	60.834	-0.010	-0.943	1.213	-1.871
G37	9.463	122.888	176.017	48.228	0.691	9.304	1.387	2.979
G38	8.691	102.408	171.627	45.534	0.315	-6.322	-2.270	0.540
V39	6.612	118.628	172.740	59.051	-1.559	-1.511	-3.334	-3.253
V40	8.240	124.379	176.993	63.193	-0.297	-2.239	1.035	0.809
I41	8.529	126.958	175.206	60.403	-0.028	-1.027	0.237	-0.468

$A\beta^{1-42-K28E}$

Res.	δ_f ($^1H^N$)	δ_f (^{15}N)	δ_f ($^{13}C'$)	δ_f ($^{13}C^\alpha$)	$\delta_f - \delta_u$ ($^1H^N$)	$\delta_f - \delta_u$ (^{15}N)	$\delta_f - \delta_u$ ($^{13}C'$)	$\delta_f - \delta_u$ ($^{13}C^\alpha$)
I32	7.259	117.613	177.074	62.459	-1.257	-9.615	0.337	1.265
G33	7.526	106.533	172.206	45.862	-1.152	-7.298	-1.670	0.763
L34	7.574	121.419	174.487	54.647	-0.628	-0.511	-2.914	-0.553
M35	7.978	121.249	177.100	53.778	-0.601	-0.974	1.004	-1.570
V36	8.259	121.099	177.947	61.068	-0.168	-2.054	1.164	-1.637
G37	9.251	121.178	175.764	47.886	0.479	7.594	1.134	2.637
G38	8.603	103.216	171.637	45.512	0.227	-5.514	-2.260	0.518
V39	6.736	118.679	173.073	59.497	-1.435	-1.460	-3.001	-2.807
V40	8.196	124.667	176.907	63.103	-0.341	-1.951	0.949	0.719
I41	8.483	127.161	175.181	60.571	-0.074	-0.824	0.212	-0.300

$A\beta^{1-42-Ox}$

Res.	δ_f ($^1H^N$)	δ_f (^{15}N)	δ_f ($^{13}C'$)	δ_f ($^{13}C^\alpha$)	$\delta_f - \delta_u$ ($^1H^N$)	$\delta_f - \delta_u$ (^{15}N)	$\delta_f - \delta_u$ ($^{13}C'$)	$\delta_f - \delta_u$ ($^{13}C^\alpha$)
I32	6.954	117.008	175.775	61.043	-1.562	-10.220	-0.962	-0.151
G33	7.248	106.940	172.232	45.139	-1.430	-6.891	-1.644	0.040
L34	7.399	121.584	174.699	54.144	-0.828	-0.243	-2.824	-1.066
M35	8.077	120.997	176.962	50.782	-0.670	-0.561	1.827	-4.359
V36	7.605	117.340	177.861	60.742	-0.947	-5.898	1.135	-1.975
G37	8.807	115.804	173.562	45.586	0.035	2.220	-1.068	0.337
G38	8.765	107.330	171.866	44.809	0.389	-1.400	-2.031	-0.185
V39	7.320	117.717	174.753	60.412	-0.851	-2.422	-1.321	-1.892
V40	8.039	124.683	176.479	62.847	-0.498	-1.935	0.521	0.463
I41	8.272	126.507	175.105	60.563	-0.285	-1.478	0.136	-0.308

Table S3 -CONTINUED-

$A\beta^{1-40}$

Res.	δ_f ($^1H^N$)	δ_f (^{15}N)	δ_f ($^{13}C'$)	δ_f ($^{13}C^\alpha$)	$\delta_f - \delta_u$ ($^1H^N$)	$\delta_f - \delta_u$ (^{15}N)	$\delta_f - \delta_u$ ($^{13}C'$)	$\delta_f - \delta_u$ ($^{13}C^\alpha$)
I32	6.859	118.022	176.153	61.304	-1.657	-9.206	-0.584	0.110
G33	7.275	106.947	172.211	45.578	-1.403	-6.884	-1.665	0.479
L34	7.520	120.228	177.449	54.422	-0.682	-1.702	0.048	-0.778
M35	8.209	120.997	177.719	54.529	-0.370	-1.226	1.623	-0.819
V36	7.379	115.789	176.249	60.987	-1.048	-7.364	-0.534	-1.718
G37	7.801	110.307	173.041	44.479	-0.971	-3.277	-1.589	-0.770
G38	8.021	110.459	171.921	45.777	-0.355	1.729	-1.976	0.783
V39	7.926	118.202	174.169	61.563	-0.270	-2.011	-1.567	-1.004

$A\beta^{1-40-Ox}$

Res.	δ_f ($^1H^N$)	δ_f (^{15}N)	δ_f ($^{13}C'$)	δ_f ($^{13}C^\alpha$)	$\delta_f - \delta_u$ ($^1H^N$)	$\delta_f - \delta_u$ (^{15}N)	$\delta_f - \delta_u$ ($^{13}C'$)	$\delta_f - \delta_u$ ($^{13}C^\alpha$)
I32	6.889	118.290	175.975	60.742	-1.627	-8.938	-0.762	-0.452
G33	7.327	108.098	173.039	45.061	-1.351	-5.733	-0.837	-0.038
L34	7.456	120.833	176.826	54.309	-0.771	-0.994	-0.697	-0.901
M35	8.247	121.128	177.097	52.599	-0.500	-0.430	1.962	-2.542
V36	7.438	116.354	176.959	60.867	-1.114	-6.884	0.233	-1.850
G37	7.992	108.460	172.437	43.665	-0.780	-5.124	-2.193	-1.584
G38	8.330	111.536	172.653	45.529	-0.046	2.806	-1.244	0.535
V39	8.217	118.622	174.848	61.938	0.021	-1.591	-0.888	-0.629

Table S4. Comparison of calculated ΔASA for the fragments listed in Table 3**, main text.** "Folded" corresponds to the coordinates for the decapeptide excerpted from the PDB. "Unfolded" corresponds to the peptide with extended backbone torsion angles ($\phi = -120^{o}$; $\psi = 120^{o}$).

	Solvent accessible surface area (ASA, Å^2)		
PDB ID	**folded**	**unfolded**	**ΔASA**
1GRN	911	1334	423
2E7P	895	1363	468
1QBS	962	1341	379
1N0S	945	1413	468
1TVQ	928	1221	293
1VM9	925	1194	269
2NMZ	928	1341	413
2PE8	1071	1372	301
2FA4	1094	1404	310
		Average ΔASA:	**369 ± 73**

Table S5. The calculated the corresponding rms values for the 9 peptides whose structure was found to match those of the C-terminal β-hairpin. Units are in ppm.

PDB ID	rms ($^{1}H^{N}$)	rms (^{15}N)	rms ($^{13}C^{\alpha}$)	rms ($^{13}C'$)
1GRN	0.911	3.965	1.396	1.579
2EZP	1.024	4.449	1.130	1.489
1QBS	---	3.295	1.730	1.948
1N0S	0.958	5.028	1.468	1.485
1TVQ	1.147	5.237	1.720	2.010
1VM9	0.793	4.094	1.486	1.963
2NMZ	0.925	3.209	1.685	---
2PE8	0.654	5.316	2.348	---
2FA4	1.133	3.605	0.890	3.394
Average:	0.943	4.244	1.539	1.981
Standard deviation:	0.166	0.812	0.413	0.664

Table S6. Individually fitted offsets for unfolded chemical shifts (ppm) for the five Aβ peptides.

		$A\beta^{1-42}$		
res.	**$^{1}H^{N}$**	**^{15}N**	**$^{13}C'$**	**$^{13}C^{\alpha}$**
I32	0.001	-0.064	-0.195	-0.079
G33	0.027	0.520	-0.503	-0.073
L34	0.025	0.464	-0.465	-0.122
M35	0.047	-0.106	-0.056	0.054
V36	0.055	0.490	-0.140	-0.096
G37	0.019	0.209	-0.236	0.035
G38	-0.001	-0.309	-0.496	-0.047
V39	0.064	-0.184	-0.472	-0.212
V40	0.006	-0.330	0.021	0.026
I41	0.015	-0.005	-0.066	-0.058

		$A\beta^{1-42-K28E}$		
res.	**$^{1}H^{N}$**	**^{15}N**	**$^{13}C'$**	**$^{13}C^{\alpha}$**
I32	-0.015	-0.213	-0.168	-0.031
G33	0.019	0.445	-0.479	-0.051
L34	0.017	0.457	-0.456	-0.117
M35	0.043	-0.132	-0.044	0.062
V36	0.054	0.476	-0.142	-0.090
G37	0.016	0.159	-0.246	0.017
G38	-0.002	-0.289	-0.498	-0.053
V39	0.071	-0.178	-0.463	-0.182
V40	0.006	-0.318	0.018	0.031
I41	0.016	0.019	-0.066	-0.048

Table S6 -CONTINUED-

	$A\beta^{1-42-Ox}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	0.006	-0.073	-0.188	-0.063
G33	0.031	0.538	-0.385	-0.066
L34	0.029	0.505	-0.319	-0.049
M35	0.051	0.048	-0.070	0.114
V36	0.037	0.366	-0.157	-0.084
G37	0.006	-0.177	-0.303	-0.087
G38	0.008	-0.192	-0.437	-0.092
V39	0.117	-0.198	-0.403	-0.146
V40	0.003	-0.349	0.008	0.037
I41	0.014	0.051	-0.064	-0.045

	$A\beta^{1-40}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.025	-0.124	-0.195	-0.073
G33	0.008	0.493	-0.470	-0.081
L34	0.008	0.377	-0.356	-0.111
M35	0.033	-0.305	-0.015	0.094
V36	0.046	0.297	-0.176	-0.102
G37	-0.009	-0.102	-0.302	-0.084
G38	-0.014	-0.147	-0.526	-0.039
V39	0.099	-0.133	-0.806	0.062

	$A\beta^{1-40-Ox}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	0.002	-0.012	-0.174	-0.078
G33	0.035	0.603	-0.352	-0.071
L34	0.026	0.476	-0.280	-0.045
M35	0.045	-0.041	-0.064	0.153
V36	0.048	0.358	-0.163	-0.094
G37	0.010	-0.262	-0.301	-0.109
G38	0.003	-0.152	-0.463	-0.056
V39	0.120	-0.093	-0.762	0.105

Table S7. Averaged offsets for unfolded chemical shifts (ppm) used in constrained fitting. For the final fitting the unfolded shifts were fixed to averaged values among corresponding residues obtained from initial peptide-specific fits (Table S6). For residues 32, 33, 37, 38, 40, and 41 shifts were averaged over all the peptides; for residues 34, 35, and 36, the shifts of the two Met-35 oxidized peptides were averaged separately; for residue 39, the shifts of the two $A\beta^{1-42}$ peptides were averaged separately. Units are ppm.

	$A\beta^{1-42}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.006	-0.097	-0.184	-0.065
G33	0.024	0.520	-0.438	-0.068
L34	0.017	0.433	-0.426	-0.117
M35	0.041	-0.181	-0.038	0.070
V36	0.052	0.421	-0.153	-0.096
G37	0.008	-0.035	-0.278	-0.046
G38	-0.001	-0.218	-0.484	-0.057
V39	0.084	-0.186	-0.446	-0.180
V40	0.005	-0.332	0.016	0.032
I41	0.015	0.022	-0.065	-0.050

	$A\beta^{1-42-K28E}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.006	-0.097	-0.184	-0.065
G33	0.024	0.520	-0.438	-0.068
L34	0.017	0.433	-0.426	-0.117
M35	0.041	-0.181	-0.038	0.070
V36	0.052	0.421	-0.153	-0.096
G37	0.008	-0.035	-0.278	-0.046
G38	-0.001	-0.218	-0.484	-0.057
V39	0.084	-0.186	-0.446	-0.180
V40	0.005	-0.332	0.016	0.032
I41	0.015	0.022	-0.065	-0.050

Table S7 -CONTINUED-

	$A\beta^{1-42-Ox}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.006	-0.097	-0.184	-0.065
G33	0.024	0.520	-0.438	-0.068
L34	0.028	0.491	-0.300	-0.047
M35	0.048	0.003	-0.067	0.133
V36	0.043	0.362	-0.160	-0.089
G37	0.008	-0.035	-0.278	-0.046
G38	-0.001	-0.218	-0.484	-0.057
V39	0.084	-0.186	-0.446	-0.180
V40	0.005	-0.332	0.016	0.032
I41	0.015	0.022	-0.065	-0.050

	$A\beta^{1-40}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.006	-0.097	-0.184	-0.065
G33	0.024	0.520	-0.438	-0.068
L34	0.017	0.433	-0.426	-0.117
M35	0.041	-0.181	-0.038	0.070
V36	0.052	0.421	-0.153	-0.096
G37	0.008	-0.035	-0.278	-0.046
G38	-0.001	-0.218	-0.484	-0.057
V39	0.109	-0.113	-0.784	0.083

	$A\beta^{1-40-Ox}$			
res.	$^{1}H^{N}$	^{15}N	$^{13}C'$	$^{13}C^{\alpha}$
I32	-0.006	-0.097	-0.184	-0.065
G33	0.024	0.520	-0.438	-0.068
L34	0.028	0.491	-0.300	-0.047
M35	0.048	0.003	-0.067	0.133
V36	0.043	0.362	-0.160	-0.089
G37	0.008	-0.035	-0.278	-0.046
G38	-0.001	-0.218	-0.484	-0.057
V39	0.109	-0.113	-0.784	0.083

References

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