**Supplemental Data**

**Table S1.** $^{15}N$ and $^{1}H$ temperature coefficients of backbone amide sides in [*U*-$^{15}N$] synthetic elastin.

| | Temperature coefficient (ppb/K) | |
|---|---|---|
| Peak No. | $^{15}N$ | $^{1}H$ |
| 1 | -32 +/- 7 | -5.6 +/- 2.0 |
| 2 | -7 +/- 5 | -2.3 +/- 2.3 |
| 3 | -20 +/- 4 | -5.1 +/- 3.0 |
| 4 | -35 +/- 7 | -4.7 +/- 3.2 |
| 5 | -32 +/- 7 | -5.0 +/- 2.6 |
| 6 | -40 +/- 21 | -5.3 +/- 3.4 |
| 7 | -14 +/- 3 | -4.2 +/- 2.8 |

**Table S2.** Three-residue sequences and their occurrences in tropoelastin.

| $R_{-1}$-Gly-$R_{+1}$ | | | | | | $R_{-1}$-Ala-$R_{+1}$ | | | | $R_{-1}$-Val-$R_{+1}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PGV | 26 | AGV | 9 | FGL | 3 | AAA | 38 | VAP | 6 | GVG | 31 | PVP | 1 |
| PGG | 12 | AGL | 8 | FGA | 2 | AAK | 21 | VAA | 3 | GVP | 17 | PVV | 1 |
| PGA | 11 | AGA | 5 | FGG | 1 | AAG | 6 | VAG | 2 | GVA | 11 | PVX | 2 |
| PGF | 4 | AGI | 4 | FGP | 1 | AAQ | 2 | VAD | 1 | GVL | 5 | | |
| PGL | 3 | AGG | 1 | FGV | 1 | AAV | 2 | VAX | 12 | GVV | 3 | | |
| PGI | 2 | AGK | 1 | FGX | 8 | AAR | 1 | | | GVK | 2 | | |
| PGK | 1 | AGP | 1 | | | AAY | 1 | LAA | 1 | GVF | 1 | | |
| PGX | 59 | AGQ | 1 | TGA | 1 | AAX | 71 | LAG | 1 | GVS | 1 | | |
| | | AGY | 1 | TGK | 1 | | | LAP | 1 | GVY | 1 | | |
| GGV | 14 | AGX | 31 | TGT | 1 | GAG | 17 | LAX | 3 | GVX | 72 | | |
| GGL | 6 | | | TGV | 1 | GAA | 7 | | | | | | |
| GGA | 5 | LGG | 9 | TGX | 4 | GAL | 5 | PAA | 4 | AVP | 3 | | |
| GGI | 4 | LGV | 6 | | | GAF | 2 | PAV | 1 | AVT | 1 | | |
| GGP | 2 | LGA | 5 | IGG | 1 | GAI | 2 | PAX | 5 | AVV | 1 | | |
| GGF | 1 | LGK | 1 | IGP | 1 | GAR | 2 | | | AVX | 5 | | |
| GGG | 1 | LGP | 1 | IGX | 2 | GAV | 2 | EAA | 1 | | | | |
| GGK | 1 | LGY | 1 | | | GAC | 1 | EAQ | 1 | VVG | 2 | | |
| GGY | 1 | LGX | 23 | | | GAX | 38 | EAX | 2 | VVP | 2 | | |
| GGX | 35 | | | | | | | | | VVS | 1 | | |
| | | YGA | 4 | | | KAA | 12 | QAA | 2 | VVX | 5 | | |
| VGV | 13 | YGV | 2 | | | KAG | 2 | | | | | | |
| VGG | 9 | YGL | 1 | | | KAP | 2 | SAA | 1 | LVP | 3 | | |
| VGA | 5 | YGP | 1 | | | KAC | 1 | SAG | 1 | LVG | 1 | | |
| VGI | 2 | YGY | 1 | | | KAQ | 1 | SAX | 2 | LVX | 4 | | |
| VGL | 2 | YGX | 9 | | | KAX | 18 | | | | | | |
| VGP | 2 | | | | | | | DAA | 1 | KVA | 1 | | |
| VGT | 2 | | | | | | | IAG | 1 | KVP | 1 | | |
| VGX | 35 | | | | | | | RAA | 1 | KVX | 2 | | |
| | | | | | | | | FAG | 1 | | | | |

**Figure S1.** Pulse sequence for the "semi-constant time" 2D $^{1}$H -$^{15}$N rINEPT-HETCOR experiment (Ref. S1). $^{1}$H chemical shift evolves *via* incrementation of $t_{1a}$, and the spectral width in the $^{1}$H indirect dimension was 2400 Hz. The $t_{1b}$ delay was defined as $t_{1b} = t_{1a} - 2\tau$. The delay $\tau$ was set to 1.6 ms. The phase of the first $^{1}$H 90º pulse was incremented via the States method (Ref. S2). The phase cycling scheme was $\varphi1:[+x]_8\ [-x]_8$; $\varphi2:[+x\ -x]$; $\varphi3:[+y\ -y]$; $\varphi4:[+x]_4\ [+y]_4\ [-x]_4\ [-y]_4$; $\varphi5:[+x\ -x]_2\ [+y\ -y]_2$; $\varphi rec:[+x]_2\ [-x]_2\ [+y]_2\ [-y]_2$ (Ref. S3).

**Figure S2.** Spin rate dependence of $^{15}$N rINEPT (A) and $^{1}$H MAS (B) spectra. Dependence of spectral intensities on $\nu_r$ for $^{15}$N rINEPT spectra is shown in (C).

**Figure S3.** Detailed illustration of the calculated contour plot, using Ref. S4 (denatured peptide measurements). (A) The black lines point to the calculated $^{15}$N and $^{1}$H chemical shifts for the indicated 3-aa sequences. A Gaussian is centered at each set of chemical shift values and is weighted by the relative number of occurrences of the 3-aa sequence in tropoelastin (given in parentheses). "Peaks" result from overlap of chemical shifts with little or no differences and/or high occurrences of 3-aa sequences in tropoelastin. (B) Color contours only. Numbers in parentheses give the total number of occurrences for these sequences in tropoelastin.

**Figure S4.** Comparison of calculated and experimental (5 °C) chemical shifts, using the semi-empirical methods of Refs. S4 (denatured peptide) and S5 (compiled database information). Comparisons are made with the random coil (S4A-S4D), β-strand (S4E-S4F), and the α-helix (S4G-S4H). The method using the denatured peptide (ref. S4) is used for S4A-S4B, whereas the database method (ref. S5) is used for the rest. The experimental spectra are illustrated with the grey contours. Color contours denote the calculated $^{15}$N and $^{1}$H chemical shifts for the Gly (G), Ala (A), and Val (V), with assigned amino acid in **bold**. An "X" indicates 2 or more residues in the 3$^{rd}$ position of the 3-aa sequence. The predicted "peaks" were plotted as Gaussians that are centered at the (predicted) shifts and weighted by the number of occurrences in the sequence of tropoelastin.

**References**

S1. Helmus, J. J., Surewicz, K., Surewicz, W. K., and Jaroniec, C. P. (2010) *J. Am. Chem. Soc.* **132**, 2393-2403

S2. States, D. J., Haberkorn, R. A., and Ruben, D. J. (1982) *J. Magn. Reson.* **48**, 286-292

S3. Elena, B., Lesage, A., Steuernagel, S., Bockmann, A., and Emsley, L. (2005) *J. Am. Chem. Soc.* **127**, 17296-17302

S4. Schwarzinger, S., Kroon, G. J. A., Foss, T. R., Chung, J., Wright, P. E., and Dyson, H. J. (2001) *J. Am. Chem. Soc.* **123**, 2970-2978

S5. Wang, Y. J., and Jardetzky, O. (2002) *J. Am. Chem. Soc.* **124**, 14075-14084

**Figure S1**

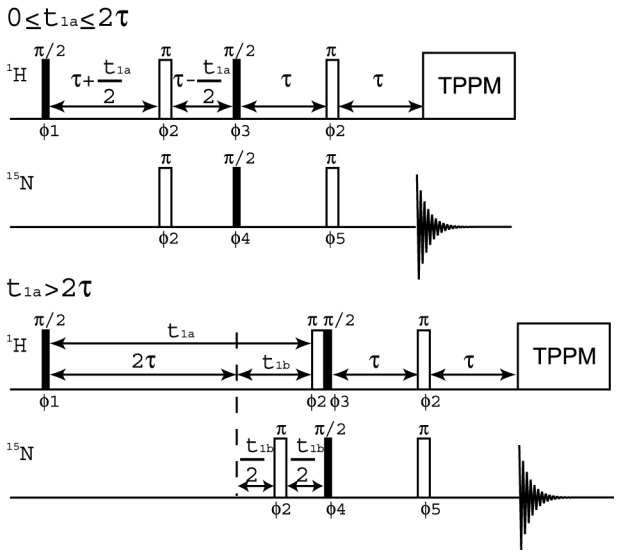

0≤t1a≤2τ
1H
15N
π/2
π
τ+ t1a/2
τ- t1a/2
τ
τ
TPPM
ϕ1
ϕ2
ϕ3
ϕ2
ϕ2
ϕ4
ϕ5
t1a>2τ
t1a
2τ
t1b
ϕ2 ϕ3
t1b/2

**Figure S2**

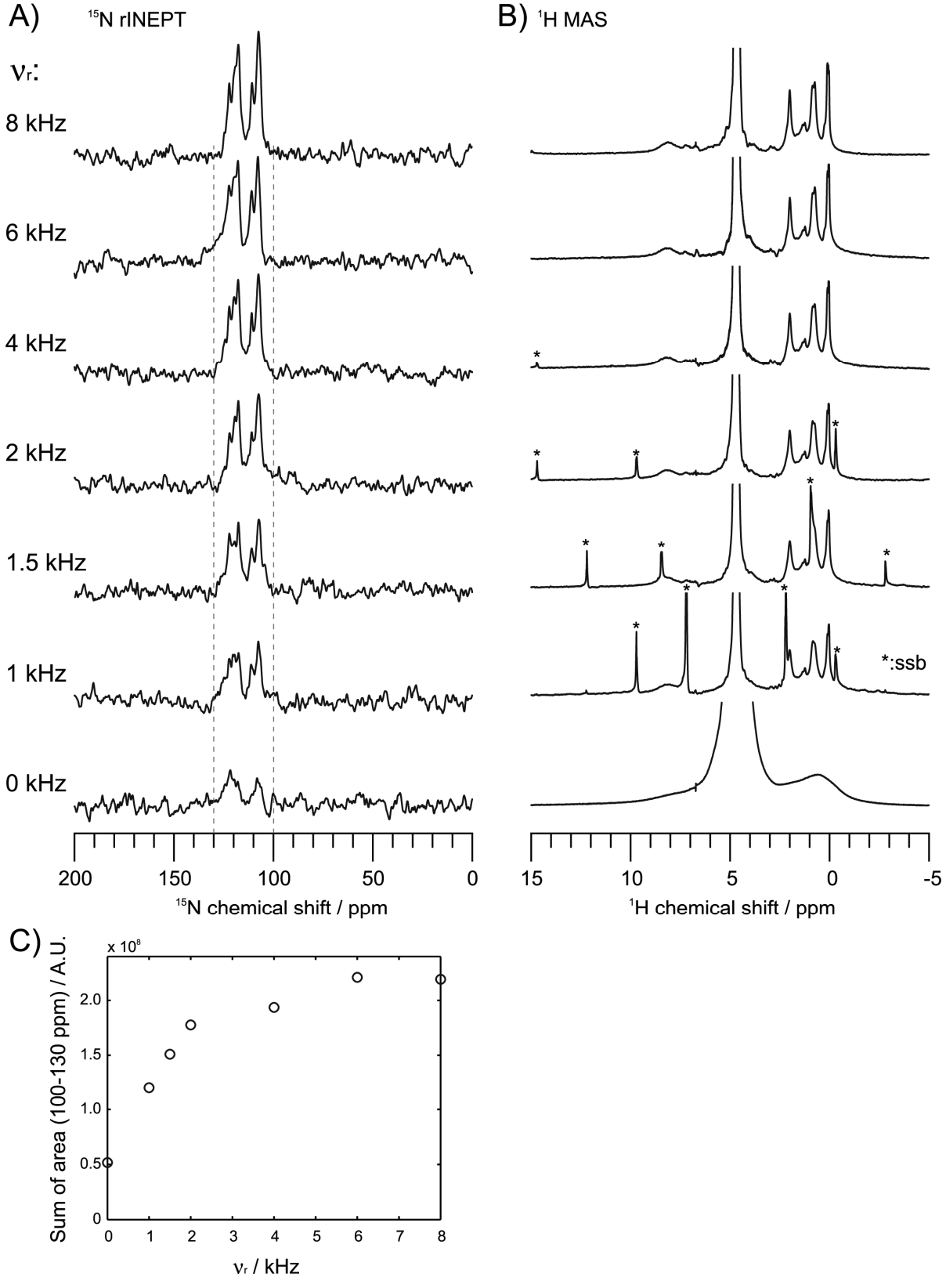

A)
15N rINEPT
νr:
8 kHz
6 kHz
4 kHz
2 kHz
1.5 kHz
1 kHz
0 kHz
200
150
100
50
0
15N chemical shift / ppm
B) 1H MAS
*:ssb
15
10
5
0
-5
1H chemical shift / ppm
C)
x 10^8
Sum of area (100-130 ppm) / A.U.
0
0.5
1.0
1.5
2.0
0
1
2
3
4
5
6
7
8
νr / kHz

**Figure S3**

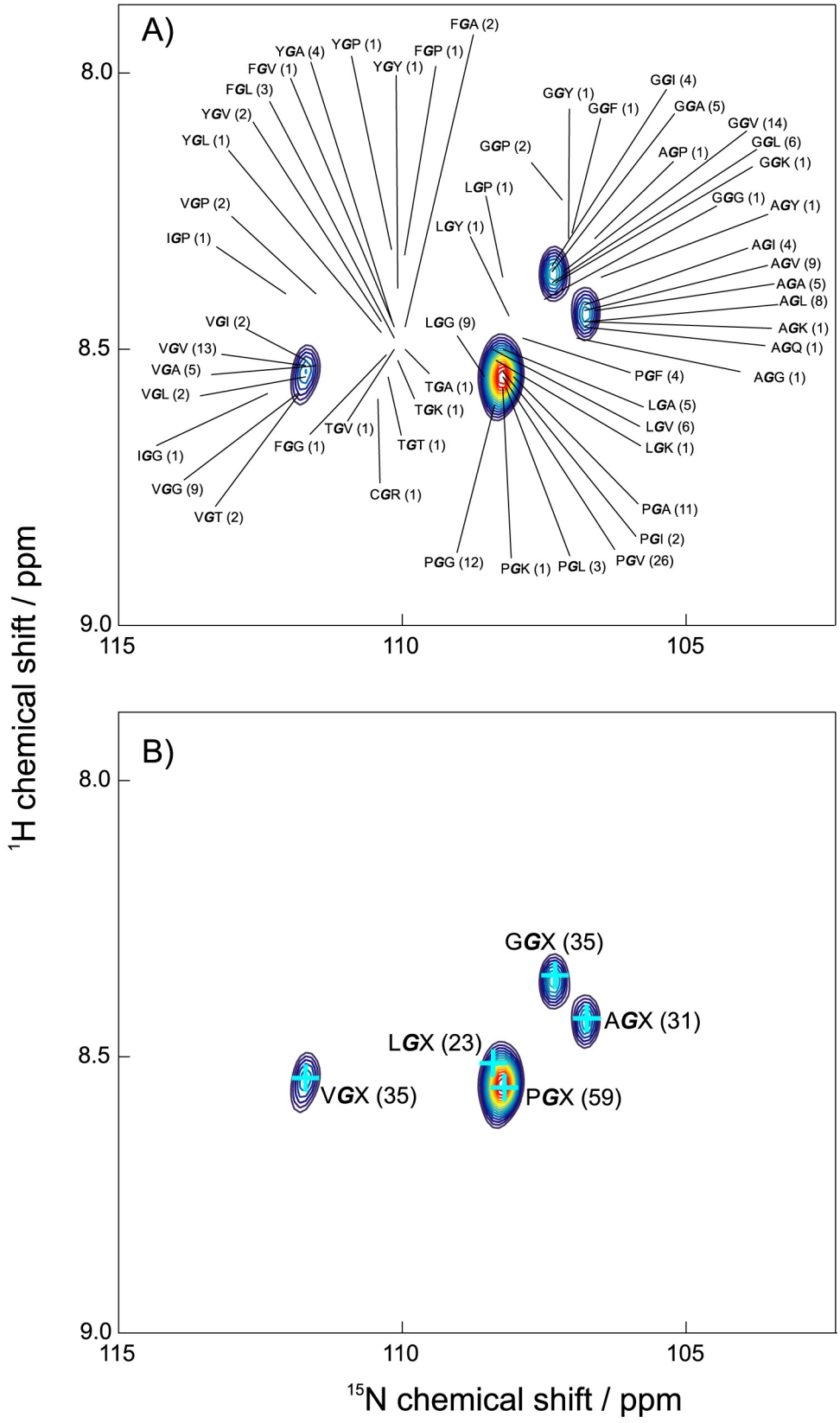
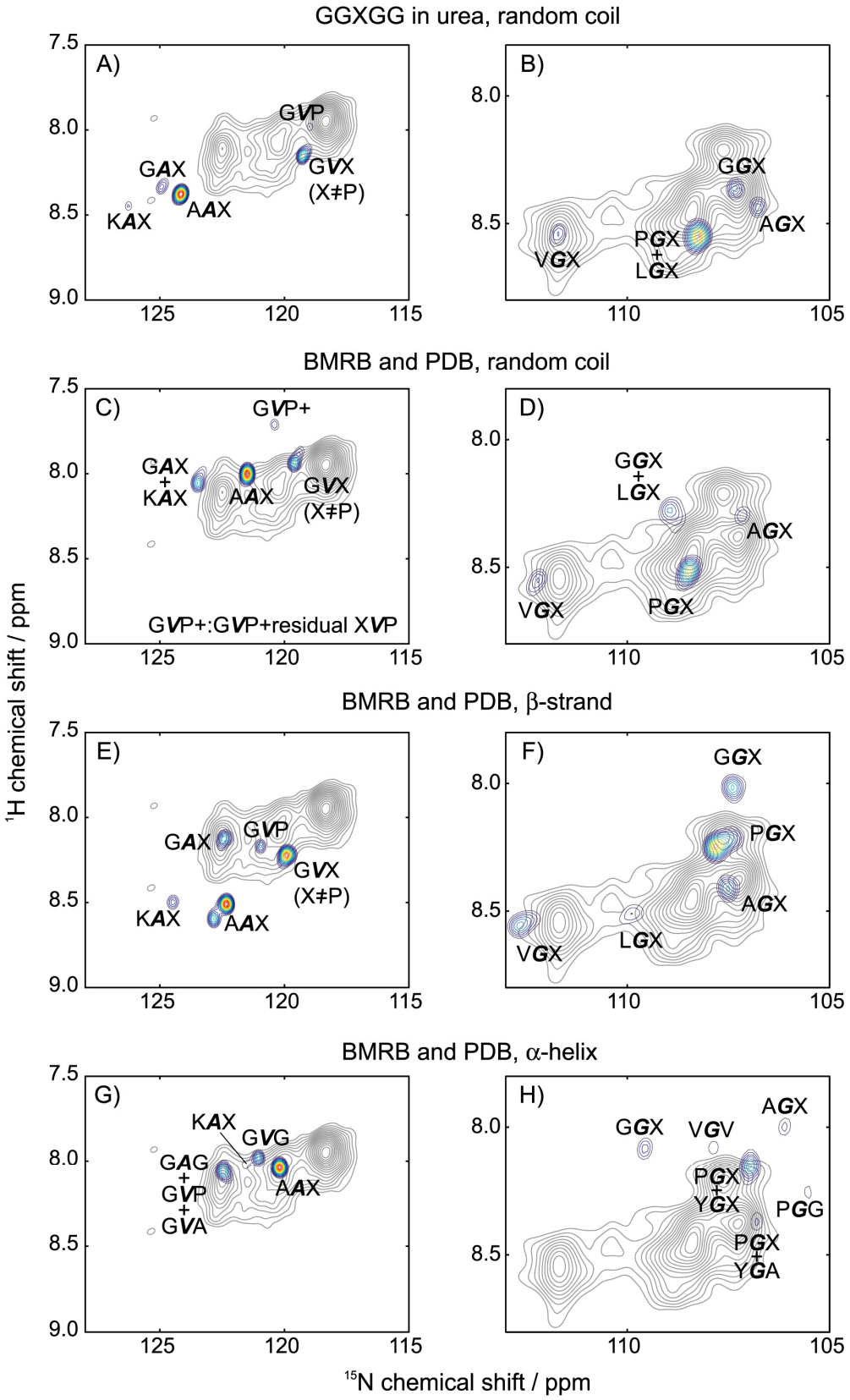

A)
B)
8.0
8.5
9.0
115
110
105
$^{1}$H chemical shift / ppm
$^{15}$N chemical shift / ppm
FGA (2)
YGA (4)
YGP (1)
FGP (1)
FGV (1)
YGY (1)
FGL (3)
YGV (2)
YGL (1)
VGP (2)
IGP (1)
VGI (2)
VGV (13)
VGA (5)
VGL (2)
IGG (1)
VGG (9)
VGT (2)
FGG (1)
TGV (1)
TGA (1)
TGK (1)
TGT (1)
CGR (1)
LGG (9)
LGP (1)
LGY (1)
PGG (12)
PGK (1)
PGL (3)
PGV (26)
PGF (4)
LGA (5)
LGV (6)
LGK (1)
PGA (11)
PGI (2)
GGY (1)
GGF (1)
GGI (4)
GGA (5)
GGV (14)
GGL (6)
GGK (1)
GGP (2)
AGP (1)
GGG (1)
AGY (1)
AGI (4)
AGV (9)
AGA (5)
AGL (8)
AGK (1)
AGQ (1)
AGG (1)
GGX (35)
AGX (31)
LGX (23)
VGX (35)
PGX (59)

**Figure S4**


GGXGG in urea, random coil
A)
GVP
GAX
GVX
(X≠P)
AAX
KAX
B)
GGX
AGX
PGX
+
LGX
VGX
BMRB and PDB, random coil
C)
GVP+
GAX
+
KAX
AAX
GVX
(X≠P)
GVP+:GVP+residual XVP
D)
GGX
+
LGX
AGX
VGX
PGX
BMRB and PDB, β-strand
E)
GAX
GVP
GVX
(X≠P)
KAX
AAX
F)
GGX
PGX
AGX
VGX
LGX
BMRB and PDB, α-helix
G)
KAX
GVG
GAG
+
GVP
+
GVA
AAX
H)
AGX
GGX
VGV
PGX
+
YGX
PGG
PGX
+
YGA
7.5
8.0
8.5
9.0
125
120
115
110
105
$^{1}$H chemical shift / ppm
$^{15}$N chemical shift / ppm