Supporting Information

A comprehensive library of blocked dipeptides reveals intrinsic backbone conformational propensities of unfolded proteins

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Experimental and SVD analysis methods

NMR. In the present work, we considered blocked dipeptides instead of normal dipeptides, where the N-terminal amino-acid is acetylated and the C-terminal amino-acid is amidated. This is mainly to avoid any possible complication induced by electrostatic interactions of terminal ammonium and carboxylate groups in an unblocked dipeptide with backbone peptides and amino-acid side-chains. For NMR experiments, we studied 361 (=19×19) dipeptides (Ac-X_{1aa}-X_{2aa}-NH_2), where Xaa represents one of the nineteen amino acids (A, C, D, E, F, G, H, I, K, L, M, N, Q, R, S, T, V, W, Y) except for proline (P). The aqueous solution pH is 2 in most cases. Among them, FF, FW, FV, FL, II, and MQ have very low solubility in water so that we were not able to obtain their NMR spectra. Due to the low solubility, we used a small amount (less than 10%) of DMSO to dissolve dipeptides that are AI, AY, CV, CY, DW, EF, EW, FA, FC, FI, FM, FN, FQ, FT, FY, IF, IM, IT, IV, IW, IY, LF, LI, LV, LW, MF,

MI, ML, MM, MY, NY, QF, QY, SF, SI, TF, TI, TW, VF, VI, VV, VW, WA, WC, WF, WI, WL, WN, WV, YF, YI, YL, YM, YN, YV). In the cases of QI, QV, MV, IL, and VC, we recorded their NMR spectra. However, since more than 10% of DMSO was used to dissolve them in water, we excluded their NMR data for subsequent population analyses. The two backbone amide proton NMR peaks of HH, KH, and TH dipeptides were found to significantly overlap with the N-H proton peak of the histidine imidazole ring at 8.61 ppm so that we also excluded these three dipeptides for subsequent conformational distribution analyses.

For those dipeptides containing acidic residues, the aqueous solution pH was controlled to be in the range from 4.1 to 5.0. The solution pH was adjusted by adding a small amount of 0.3 M HCl or 0.5 M NaOH solution to the dipeptide solution. In this pH range, the side chain COOH group becomes COO^-, which is the actual ionic state of the peptides at physiological conditions. For the dipeptides DI and DK, we needed to further lower the pH to observe the peptide N H peaks, otherwise they couldn't be identified in the NMR spectra. Therefore, in these two cases, the ionic state of the side chain differs from that at physiological condition. We therefore excluded these two dipeptides in the PII (β-strand) conformational distribution analysis. In addition, among the dipeptides containing either D or E amino acid, seventeen dipeptides including AD, CD, DD, FD, KD, LD, ND, QD, RD, TD, VD, WD, YD, EC, EH, SE, and LE show one or two minor N-H peaks. However, on the basis of the integrated peak areas of those minor peaks, those minor conformer populations should be relatively small compared to those of the two major conformers, i.e., P_{II} and β-strand.

Finally, the GG dipeptide was not included in the NMR experiments. Consequently, we analyzed 344 dipeptides, which include GX and XG systems (36 entries), in total. When we calculated the relative PII (β-strand) populations, 308 dipeptide systems except for all the XG and GX dipeptides were taken into consideration.

Singular value decomposition (SVD) method. In the present cases of the dipeptides, we measured the temperature-dependent CD spectra of all the dipeptides, $\Delta A_{\exp}(\lambda,T)$. For a given dipeptide solution with concentration of c_{dipep}, the mathematical SVD analysis of $\Delta A_{\exp}(\lambda,T)$ converts the matrix form of concentration-normalized spectrum into a product of

eigenspectra, singular value, and purely T-dependent function as

$$\overline{\Delta A}_{\exp}(\lambda,T) \equiv \Delta A_{\exp}(\lambda,T)/c_{trialanine} = \begin{bmatrix}\Delta A_1(\lambda) & \Delta A_2(\lambda)\end{bmatrix}\begin{bmatrix}C_1 & 0\\ 0 & C_2\end{bmatrix}\begin{bmatrix}f_1(T)\\ f_2(T)\end{bmatrix}$$

$$= \Delta A_1(\lambda)C_1 f_1(T) + \Delta A_2(\lambda)C_2 f_2(T), \qquad \text{(S1)}$$

where $\Delta A_1(\lambda)$ and $\Delta A_2(\lambda)$ are the SVD-eigenspectra of the two dominant conformers, respectively. The singular value matrix $\tilde{C}$ obtained from a standard SVD analysis has N different diagonal elements with N being the number of experimentally varied temperatures. However, for a two-species system, the first two singular values are significantly larger than the remaining diagonal elements. Here, the singular values C_1 and C_2 represent the relative weights of the contributions from the two components in this case. Finally, the T-dependent functions *f*(*T*) provide information on the relative population changes of the two components with respect to temperature. However, one cannot directly interpret the values $C_1 f_1(T)$ and $C_2 f_2(T)$ at a given temperature *T* as the mole fractions of the two species at all. This is because the eigenspectra $\Delta A_1(\lambda)$ and $\Delta A_2(\lambda)$ are *not* the molar CD spectra of the two chemical species but just mathematically determined eigenspectra of the two components from the SVD analysis. Therefore, there should be a proper set of criteria to obtain molar eigenspectra and relative populations. In this regard, one of the most important observations is that there are one or two isodichroic points in a number of temperature-dependent CD spectra of dipeptides. We found that the raw eigenspectra $\Delta A_1(\lambda)$ and $\Delta A_2(\lambda)$ directly obtained from the above SVD analysis usually do not meet this isodichroic-point-criterion. Thus, we found it necessary to modify the SVD procedure. As shown recently by us[1], this can be achieved by using the following 2 by 2 identity matrix,

$$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} = \begin{bmatrix}\cos\vartheta & \sin\vartheta\\ -\sin\vartheta & \cos\vartheta\end{bmatrix}\begin{bmatrix}\cos\vartheta & -\sin\vartheta\\ \sin\vartheta & \cos\vartheta\end{bmatrix} = U^{-1}(\vartheta)U(\vartheta). \qquad \text{(S2)}$$

Inserting this identity matrix into Eq.(9), we can rewrite the equation as

$$\overline{\Delta A}_{\exp}(\lambda,T)=\begin{bmatrix}\Delta A_1(\lambda) & \Delta A_2(\lambda)\end{bmatrix}U^{-1}(\vartheta)U(\vartheta)\begin{bmatrix}C_1 & 0\\ 0 & C_2\end{bmatrix}\begin{bmatrix}f_1(T)\\ f_2(T)\end{bmatrix}. \qquad \text{(S3)}$$

Note that the rotation angle ϑ is considered to be a variational parameter in this case. Then, properly adjusting ϑ, we could obtain the transformed eigenspectra satisfying the isodichroic-point-criterion. Thus, we have

$$\Delta A_{\exp}(\lambda,T)=\Delta A_{P_{II}}(\lambda)\,f_{P_{II}}(T)+\Delta A_{\beta}(\lambda)\,f_{\beta}(T), \qquad \text{(S3)}$$

where

$$\Delta A_{P_{II}}(\lambda)=\Delta\tilde{A}_1(\lambda)\cos\vartheta+\Delta\tilde{A}_2(\lambda)\sin\vartheta$$

$$\Delta A_{\beta}(\lambda)=-\Delta\tilde{A}_1(\lambda)\sin\vartheta+\Delta\tilde{A}_2(\lambda)\cos\vartheta$$

$$f_{P_{II}}(T)=C_1 f_1(T)\cos\vartheta-C_2 f_2(T)\sin\vartheta$$

$$f_{\beta}(T)=C_1 f_1(T)\sin\vartheta+C_2 f_2(T)\cos\vartheta. \qquad \text{(S4)}$$

Note that $\Delta A_{P_{II}}(\lambda)=\Delta A_{\beta}(\lambda)$ at the wavelength λ_{id} of the isodichroic point. However, still one cannot conclude that the above $\Delta A_{P_{II}}(\lambda)$ and $\Delta A_{\beta}(\lambda)$ are the molar CD spectra of the P_{II} and β-strand conformers yet, because they are not properly weighted by the molar ellipticity ratio, $R_{P_{II}/\beta}$. With this additional variational parameter, Eq.(S3) should be rewritten as

$$\Delta A_{\exp}(\lambda,T)=\frac{R_{P_{II}/\beta}}{1+R_{P_{II}/\beta}}\Delta A_{P_{II}}(\lambda)\,f_{P_{II}}(T)+\frac{1}{1+R_{P_{II}/\beta}}\Delta A_{\beta}(\lambda)\,f_{\beta}(T)$$

$$=\Delta\tilde{A}_{P_{II}}(\lambda)P_{P_{II}}(T)+\Delta\tilde{A}_{\beta}(\lambda)P_{\beta}(T). \qquad \text{(S5)}$$

Due to the newly multiplied constants $R_{P_{II}/\beta}/(1+R_{P_{II}/\beta})$ and $1/(1+R_{P_{II}/\beta})$ to the first and second *terms* in Eq.(S5), in general the two eigenspectra $\Delta\tilde{A}_{P_{II}}(\lambda)$ and $\Delta\tilde{A}_{\beta}(\lambda)$ will not satisfy the isodichroic-point-criterion, i.e., $\Delta\tilde{A}_{P_{II}}(\lambda_{id})=\Delta\tilde{A}_{\beta}(\lambda_{id})$ at the wavelength λ_{id} of the isodichroic point. Thus, one should re-adjust the rotation angle ϑ and repeat this

calculation procedure. In Ref.12(main text), we further developed a self-consistent procedure for determining the CD eigenspectra and NMR reference coupling constants of trialanine P_{II} and β-strand conformers as well as the thermodynamic properties such as ΔH and ΔS. It can be summarized as the following; (i) carry out the conventional SVD analysis of concentration-normalized $\Delta\tilde{A}_{\exp}(\lambda,T)$ to obtain the raw eigenspectra $\Delta\tilde{A}_1(\lambda)$ and $\Delta\tilde{A}_2(\lambda)$, (ii) guess $R_{P_{II}/\beta}$ value, (iii) adjust ϑ to meet the isodichroic-point-criterion, (iv) carry out the van't Hoff analysis of the temperature-dependent equilibrium constants $K_{eq}(T)$ to determine ΔH and ΔS associated with the $P_{II}\rightarrow\beta$ transition, (v) compare these ΔH and ΔS values obtained from the temperature-dependent NMR studies with those from the CD studies using the relative populations of P_{II} and β-strand, (vi) if they are not in good agreements with each other, go back to the step (ii) and repeat the calculation procedure until the results converge in a self-consistent manner. Only then, the temperature-dependent functions in Eq.(S5) correspond to the temperature-dependent populations (concentrations) of the two conformers.

Table S1: The smaller coupling constant (in Hz) among the two $^{3}J_{HN\alpha}$ values of each dipeptide. In the cases of GX and XG dipeptides, the coupling constant at the glycine residue is given here. In this table, there are nine blanks that correspond to FF, FL, FV, FW, II, MQ, HH, TH, and KH. The first six dipeptides among the nine are not soluble in water. In the latter three cases, the peptide amino proton NMR peaks overlap with the imidazole N-H peak so that the coupling constants couldn't be determined.

	C-terminal amino acid																		
	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	5.64 ±0.001	6.58 ±0.016	5.62 ±0.001	6.82 ±0.001	5.89 ±0.001	5.9 ±0.006	5.5 ±0.008	6.23 ±0.012	7.21 ±0.001	5.92 ±0.001	5.63 ±0.021	5.52 ±0.012	5.52 ±0.011	5.31 ±0.009	6.12 ±0.001	5.64 ±0.01	5.75 ±0.021	5.74 ±0.001	6.1 ±0.01
C	6.09 ±0.001	6.86 ±0.017	6.95 ±0.001	7 ±0.017	7.34 ±0.011	5.36 ±0.005	6.79 ±0.001	7.47 ±0.01	6.73 ±0.001	7.11 ±0.011	6.86 ±0.011	6.88 ±0.007	6.84 ±0.012	6.69 ±0.001	7.05 ±0.001	6.97 ±0.001	7.13 ±0.001	6.99 ±0.001	7.34 ±0.009
D	6.34 ±0.007	7.11 ±0.011	6.93 ±0.005	6.76 ±0.001	7.25 ±0.005	5.92 ±0.001	6.49 ±0.001	6.99 ±0.001	6.69 ±0.009	6.73 ±0.001	6.64 ±0.001	6.75 ±0.001	6.53 ±0.001	6.46 ±0.015	6.83 ±0.008	6.67 ±0.002	6.74 ±0.015	7.11 ±0.016	7.33 ±0.001
E	6.03 ±0.001	6.57 ±0.011	6.56 ±0.008	6.54 ±0.013	6.64 ±0.001	5.84 ±0.006	6.14 ±0.009	6.64 ±0.008	6.42 ±0.001	6.46 ±0.009	6.42 ±0.001	6.37 ±0.001	6.31 ±0.001	6.22 ±0.001	6.45 ±0.014	6.51 ±0.017	6.72 ±0.001	6.34 ±0.006	6.59 ±0.001
F	6.93 ±0.009	6.72 ±0.001	6.89 ±0.001	6.69 ±0.001		5.81 ±0.001	6.53 ±0.001	6.87 ±0.009	6.31 ±0.001		6.57 ±0.001	6.8 ±0.013	6.45 ±0.011	6.27 ±0.001	6.87 ±0.013	6.71 ±0.001			7.35 ±0.016
G	5.68 ±0.001	5.71 ±0.001	5.71 ±0.016	5.83 ±0.001	5.73 ±0.001	5.89 ±0.001	5.71 ±0.001	5.81 ±0.008	5.74 ±0.001	5.69 ±0.014	5.72 ±0.001	5.74 ±0.011	5.68 ±0.001	5.74 ±0.001	4.97 ±0.001	5.71 ±0.001	5.75 ±0.008	5.77 ±0.014	5.37 ±0.002
H	6.06 ±0.001	7.3 ±0.003	7.2 ±0.001	6.76 ±0.001	7.69 ±0.002	5.71 ±0.006		7.2 ±0.001	7.11 ±0.019	7.23 ±0.001	7.3 ±0.001	7.49 ±0.012	7.13 ±0.001	7.66 ±0.002	7.08 ±0.001	7.41 ±0.001	7.24 ±0.008	7.37 ±0.001	7.71 ±0.001
I	6.15 ±0.001	7.1 ±0.01	7.08 ±0.005	6.94 ±0.001	7.43 ±0.015	5.81 ±0.001	6.89 ±0.011		6.99 ±0.001	7.31 ±0.012	7.11 ±0.014	6.73 ±0.009	6.97 ±0.012	6.96 ±0.007	7.13 ±0.001	7.35 ±0.012	7.44 ±0.012	7 ±0.012	7.4 ±0.019

K	6.02 ±0.001	6.51 ±0.003	6.24 ±0.006	6.41 ±0.001	6.6 ±0.001	5.48 ±0.001		6.58 ±0.001	6.36 ±0.001	6.49 ±0.001	6.48 ±0.005	6.39 ±0.013	6.37 ±0.001	6.42 ±0.002	6.6 ±0.001	6.58 ±0.001	6.6 ±0.009	6.32 ±0.01	6.6 ±0.001
L	6.18 ±0.011	6.46 ±0.003	6.49 ±0.009	6.45 ±0.008	6.76 ±0.014	5.85 ±0.001	6.23 ±0.001	6.6 ±0.01	6.35 ±0.001	6.68 ±0.001	6.42 ±0.006	6.28 ±0.001	6.37 ±0.001	6.3 ±0.001	6.68 ±0.001	6.54 ±0.001	6.84 ±0.014	6.52 ±0.012	6.47 ±0.001
M	6.12 ±0.009	6.72 ±0.01	6.81 ±0.009	6.71 ±0.001	6.86 ±0.007	5.91 ±0.005	6.55 ±0.009	6.89 ±0.014	6.54 ±0.001	6.72 ±0.001	6.69 ±0.009	6.59 ±0.001		6.52 ±0.001	6.78 ±0.001	6.76 ±0.001	6.95 ±0.001	6.52 ±0.001	6.65 ±0.001
N	6.31 ±0.016	7.16 ±0.008	7.28 ±0.009	6.98 ±0.013	7.24 ±0.001	5.88 ±0.001	7.16 ±0.001	7.24 ±0.013	7.01 ±0.012	7.16 ±0.001	7.17 ±0.001	7.29 ±0.001	6.59 ±0.001	6.99 ±0.001	7.19 ±0.007	7.27 ±0.002	7.22 ±0.01	6.54 ±0.001	7.8 ±0.013
Q	6.04 ±0.001	6.76 ±0.01	6.74 ±0.001	6.76 ±0.001	6.76 ±0.012	5.82 ±0.001	6.7 ±0.009	6.97 ±0.015	6.61 ±0.016	6.78 ±0.001	6.75 ±0.009	6.66 ±0.001	6.64 ±0.001	6.63 ±0.001	6.8 ±0.001	6.83 ±0.002	6.59 ±0.014	6.53 ±0.007	6.76 ±0.011
R	6.06 ±0.001	6.45 ±0.012	6.34 ±0.011	6.67 ±0.012	6.52 ±0.001	5.98 ±0.009	6.5 ±0.001	6.57 ±0.001	6.45 ±0.013	6.46 ±0.001	6.46 ±0.001	6.4 ±0.001	6.41 ±0.01	6.42 ±0.001	6.6 ±0.001	6.55 ±0.001	6.6 ±0.001	6.18 ±0.001	6.75 ±0.002
S	6.32 ±0.005	6.73 ±0.018	6.95 ±0.014	6.97 ±0.007	7.36 ±0.011	5.53 ±0.001	6.62 ±0.013	7.08 ±0.01	6.52 ±0.005	6.68 ±0.005	6.62 ±0.001	6.69 ±0.008	6.6 ±0.018	6.49 ±0.012	6.78 ±0.008	6.73 ±0.001	6.86 ±0.006	6.87 ±0.001	7.2 ±0.012
T	6.22 ±0.01	7.43 ±0.007	7.31 ±0.001	6.86 ±0.001	7.78 ±0.012	5.8 ±0.003		7.16 ±0.011	7.22 ±0.001	7.26 ±0.001	7.35 ±0.007	7.34 ±0.012	7.24 ±0.001	7.22 ±0.001	7.18 ±0.001	7.55 ±0.009	7.45 ±0.002	7.39 ±0.001	7.61 ±0.001
V	6.08 ±0.001	7.11 ±0.001	6.91 ±0.009	6.79 ±0.001	7.39 ±0.001	5.85 ±0.017	6.88 ±0.01	7.3 ±0.005	6.98 ±0.007	7.15 ±0.001	7.06 ±0.008	6.77 ±0.008	7.01 ±0.014	6.91 ±0.001	7.12 ±0.001	7.13 ±0.001	7.32 ±0.009	7.25 ±0.012	7.38 ±0.001
W	6.6 ±0.011	6.15 ±0.001	6.31 ±0.001	6.24 ±0.001	6.98 ±0.013	5.89 ±0.003	6.13 ±0.001	6.6 ±0.011	5.91 ±0.001	6.58 ±0.009	6.02 ±0.001	6.3 ±0.013	5.91 ±0.001	5.81 ±0.001	6.38 ±0.001	6.29 ±0.001	7.4 ±0.007	6.03 ±0.001	6.84 ±0.001
Y	6.56 ±0.001	6.52 ±0.003	6.78 ±0.001	6.71 ±0.001	7.19 ±0.012	5.88 ±0.001	6.42 ±0.001	6.8 ±0.013	6.19 ±0.001	6.63 ±0.013	6.51 ±0.001	6.71 ±0.012	6.3 ±0.002	6.12 ±0.001	6.75 ±0.001	6.63 ±0.001	6.71 ±0.015	6.62 ±0.001	7.13 ±0.001

Table S2: The larger coupling constant (in Hz) among the two $^{3}J_{HN\alpha}$ values of each dipeptide. In the cases of GX and XG dipeptides, the coupling constant at the Xaa residue is given here. In this table, there are nine blanks that correspond to FF, FL, FV, FW, II, MQ, HH, TH, and KH.

	C-terminal amino acid																		
	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	6.14 ±0.001	7.46 ±0.001	7.32 ±0.001	7.06 ±0.001	7.58 ±0.001	5.49 ±0.012	7.91 ±0.001	8.01 ±0.022	7.31 ±0.001	7.42 ±0.001	7.39 ±0.009	7.69 ±0.01	7.26 ±0.006	7.29 ±0.016	7.13 ±0.001	8 ±0.001	7.75 ±0.001	7.27 ±0.001	7.67 ±0.012
C	7.03 ±0.001	7.48 ±0.016	7.25 ±0.007	7.25 ±0.014	7.73 ±0.005	6.9 ±0.001	7.92 ±0.001	7.9 ±0.01	7.13 ±0.006	7.23 ±0.004	7.41 ±0.011	7.68 ±0.015	7.21 ±0.015	7.21 ±0.001	7.1 ±0.001	7.95 ±0.006	7.81 ±0.004	7.38 ±0.001	7.77 ±0.009
D	6.76 ±0.007	7.2 ±0.016	7.51 ±0.001	7.05 ±0.001	7.79 ±0.005	6.84 ±0.012	7.67 ±0.005	7.87 ±0.001	7.44 ±0.009	7.34 ±0.001	7.53 ±0.001	7.85 ±0.001	7.5 ±0.009	7.46 ±0.012	7.24 ±0.008	8.12 ±0.001	7.78 ±0.001	7.39 ±0.016	7.77 ±0.001
E	6.63 ±0.002	7.5 ±0.011	7.32 ±0.008	6.87 ±0.004	7.93 ±0.001	6.33 ±0.001	8.28 ±0.015	7.74 ±0.008	6.73 ±0.001	7.21 ±0.009	7.33 ±0.001	7.67 ±0.001	7.21 ±0.001	7.25 ±0.001	7.12 ±0.014	8.01 ±0.008	7.75 ±0.001	7.49 ±0.013	7.86 ±0.001
F	7.27 ±0.009	8.05 ±0.001	7.54 ±0.001	7.37 ±0.001		6.69 ±0.001	8.16 ±0.001	8.34 ±0.008	7.62 ±0.001		7.75 ±0.001	8.01 ±0.013	7.58 ±0.011	7.72 ±0.001	7.39 ±0.013	8.15 ±0.01			8.15 ±0.016
G	6.35 ±0.006	7.55 ±0.012	7.39 ±0.015	7.01 ±0.001	7.54 ±0.001	5.69 ±0.001	7.91 ±0.001	7.7 ±0.009	7.11 ±0.003	7.3 ±0.014	7.43 ±0.008	7.79 ±0.012	7.3 ±0.005	7.29 ±0.012	7.32 ±0.015	8 ±0.008	7.67 ±0.01	7.17 ±0.001	7.45 ±0.001
H	7.48 ±0.001	7.37 ±0.003	7.34 ±0.001	7.42 ±0.001	7.76 ±0.002	7.44 ±0.001		7.82 ±0.001	7.22 ±0.019	7.43 ±0.009	7.38 ±0.001	7.55 ±0.001	7.26 ±0.012	7.69 ±0.002	7.52 ±0.001	7.88 ±0.001	7.81 ±0.001	7.55 ±0.001	7.79 ±0.001
I	7.21 ±0.001	7.6 ±0.001	7.48 ±0.006	7.09 ±0.001	7.99 ±0.013	6.72 ±0.001	8.23 ±0.003		7.24 ±0.001	7.51 ±0.016	7.54 ±0.012	7.76 ±0.01	7.24 ±0.002	7.41 ±0.001	7.18 ±0.001	8.23 ±0.019	8.22 ±0.012	7.64 ±0.012	8.17 ±0.008
K	6.56	7.4	7.28	6.73	7.81	6.37		7.79	7.11	7.22	7.35	7.64	7.13	7.22	7.07	7.96	7.78	7.51	7.87

	±0.001	±0.001	±0.004	±0.001	±0.001	±0.001		±0.001	±0.001	±0.001	±0.001	±0.005	±0.001	±0.001	±0.001	±0.001	±0.009	±0.01	±0.001
L	6.58 ±0.011	7.56 ±0.001	7.33 ±0.009	6.87 ±0.001	7.93 ±0.014	6.34 ±0.01	8.1 ±0.001	8.06 ±0.013	7.3 ±0.001	7.76 ±0.001	7.5 ±0.001	7.7 ±0.001	7.3 ±0.001	7.4 ±0.001	7.24 ±0.001	8.1 ±0.001	8.12 ±0.014	8.06 ±0.015	8.02 ±0.001
M	6.81 ±0.009	7.48 ±0.01	7.2 ±0.009	7.01 ±0.001	7.81 ±0.007	6.63 ±0.011	7.51 ±0.012	7.96 ±0.014	7.17 ±0.001	7.33 ±0.001	7.45 ±0.009	7.65 ±0.001		7.29 ±0.001	7.12 ±0.001	7.99 ±0.001	8.01 ±0.001	7.53 ±0.001	7.96 ±0.001
N	7.26 ±0.016	7.63 ±0.008	7.44 ±0.009	7.27 ±0.013	7.53 ±0.001	7.27 ±0.001	8.21 ±0.002	7.83 ±0.005	7.29 ±0.012	7.32 ±0.001	7.51 ±0.005	7.8 ±0.001	7.12 ±0.001	7.38 ±0.001	7.35 ±0.007	7.69 ±0.001	7.84 ±0.001	7.54 ±0.001	7.86 ±0.017
Q	6.82 ±0.001	7.46 ±0.005	7.19 ±0.001	6.81 ±0.001	7.9 ±0.012	6.63 ±0.004	7.77 ±0.001	7.79 ±0.014	7.1 ±0.009	7.17 ±0.001	7.33 ±0.013	7.57 ±0.001	7.13 ±0.001	7.18 ±0.001	7.07 ±0.001	7.93 ±0.002	7.79 ±0.013	7.54 ±0.001	7.91 ±0.011
R	6.62 ±0.001	7.45 ±0.001	7.23 ±0.011	6.67 ±0.008	7.92 ±0.001	6.49 ±0.014	7.79 ±0.01	7.81 ±0.001	7.14 ±0.008	7.25 ±0.001	7.33 ±0.001	6.58 ±0.001	7.16 ±0.009	7.22 ±0.001	7.09 ±0.001	7.96 ±0.001	7.78 ±0.001	7.63 ±0.001	7.79 ±0.002
S	6.74 ±0.001	7.66 ±0.013	7.73 ±0.008	7.11 ±0.014	7.98 ±0.011	6.74 ±0.015	8.05 ±0.011	7.96 ±0.016	7.4 ±0.014	7.32 ±0.001	7.48 ±0.001	7.77 ±0.017	7.37 ±0.003	7.42 ±0.009	7.27 ±0.008	8.1 ±0.001	7.82 ±0.006	7.3 ±0.001	7.64 ±0.012
T	7.59 ±0.013	7.51 ±0.001	7.49 ±0.001	7.51 ±0.001	7.82 ±0.012	7.27 ±0.001		7.95 ±0.011	7.22 ±0.001	7.33 ±0.001	7.4 ±0.001	7.66 ±0.01	7.34 ±0.001	7.32 ±0.001	7.62 ±0.001	8.05 ±0.009	7.76 ±0.002	7.46 ±0.001	7.72 ±0.001
V	7.25 ±0.015	7.56 ±0.001	7.26 ±0.011	7.13 ±0.009	7.72 ±0.015	6.78 ±0.001	8.09 ±0.002	7.91 ±0.005	7.15 ±0.001	7.25 ±0.001	7.38 ±0.001	7.64 ±0.01	7.18 ±0.001	7.26 ±0.001	7.15 ±0.009	7.99 ±0.001	7.9 ±0.009	7.55 ±0.012	7.87 ±0.001
W	6.78 ±0.011	7.85 ±0.001	7.82 ±0.001	7.32 ±0.001	8.16 ±0.015	6.29 ±0.003	8.1 ±0.001	8.45 ±0.012	7.75 ±0.001	7.85 ±0.012	7.73 ±0.001	8.17 ±0.013	7.59 ±0.001	7.74 ±0.001	7.48 ±0.001	8.3 ±0.001	8.38 ±0.012	7.46 ±0.015	7.98 ±0.001
Y	6.69 ±0.001	7.92 ±0.003	7.6 ±0.001	7.16 ±0.001	8.11 ±0.012	6.56 ±0.001	8.16 ±0.001	8.29 ±0.011	7.63 ±0.001	7.71 ±0.013	7.72 ±0.001	7.99 ±0.01	7.59 ±0.002	7.74 ±0.001	7.45 ±0.001	8.22 ±0.001	8.4 ±0.016	7.63 ±0.001	8.06 ±0.001

Table S3. The average coupling constants (in Hz) $^{3}J_{HN\alpha}$. For each dipeptide, there are two N-H groups so that two $^{3}J_{HN\alpha}$ values are obtained from the NMR spectrum. The average values of the dipeptides are given in this table. Here, there are nine blanks that correspond to FF, FL, FV, FW, II, MQ, HH, TH, and KH. The first six dipeptides among the nine are not soluble in water. In the latter three cases, the peptide N-H proton NMR peaks overlap with the imidazole N-H peak so that the coupling constants couldn't be determined.

	C-terminal amino acid																		
	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	5.89 ±0.001	7.02 ±0.009	6.47 ±0.001	6.94 ±0.001	6.735 ±0.001	5.695 ±0.009	6.705 ±0.005	7.12 ±0.017	7.26 ±0.001	6.67 ±0.001	6.51 ±0.015	6.605 ±0.011	6.39 ±0.009	6.3 ±0.013	6.625 ±0.001	6.82 ±0.006	6.75 ±0.011	6.505 ±0.001	6.885 ±0.011
C	6.56 ±0.001	7.17 ±0.017	7.1 ±0.004	7.125 ±0.016	7.535 ±0.008	6.13 ±0.003	7.355 ±0.001	7.685 ±0.01	6.93 ±0.004	7.17 ±0.008	7.135 ±0.011	7.28 ±0.011	6.95 ±0.014	6.95 ±0.001	7.075 ±0.001	7.46 ±0.004	7.47 ±0.003	7.185 ±0.001	7.555 ±0.009
D	6.55 ±0.007	7.155 ±0.014	7.22 ±0.003	6.905 ±0.001	7.52 ±0.005	6.38 ±0.007	7.08 ±0.003	7.43 ±0.001	7.065 ±0.009	7.035 ±0.001	7.085 ±0.001	7.3 ±0.001	7.015 ±0.005	6.96 ±0.014	7.035 ±0.008	7.395 ±0.002	7.26 ±0.008	7.25 ±0.016	7.55 ±0.001
E	6.33 ±0.002	7.035 ±0.011	6.94 ±0.008	6.705 ±0.009	7.285 ±0.001	6.085 ±0.004	7.21 ±0.012	7.19 ±0.008	6.575 ±0.001	6.835 ±0.009	6.875 ±0.001	7.02 ±0.001	6.76 ±0.001	6.735 ±0.001	6.785 ±0.014	7.26 ±0.013	7.235 ±0.001	6.915 ±0.01	7.225 ±0.001
F	7.1 ±0.009	7.385 ±0.001	7.215 ±0.001	7.03 ±0.001		6.25 ±0.001	7.345 ±0.001	7.605 ±0.009	6.965 ±0.001		7.16 ±0.001	7.405 ±0.013	7.015 ±0.011	6.995 ±0.001	7.13 ±0.013	7.43 ±0.006			7.75 ±0.016
G	6.015 ±0.004	6.63 ±0.007	6.55 ±0.016	6.42 ±0.001	6.635 ±0.001	5.79 ±0.001	6.81 ±0.001	6.755 ±0.009	6.425 ±0.002	6.495 ±0.014	6.575 ±0.005	6.765 ±0.012	6.49 ±0.003	6.515 ±0.007	6.145 ±0.008	6.855 ±0.005	6.71 ±0.009	6.47 ±0.008	6.41 ±0.002
H	6.77 ±0.001	7.335 ±0.003	7.27 ±0.001	7.09 ±0.001	7.725 ±0.002	6.575 ±0.004		7.51 ±0.001	7.165 ±0.019	7.33 ±0.005	7.34 ±0.001	7.48 ±0.007	7.195 ±0.007	7.675 ±0.002	7.3 ±0.001	7.645 ±0.001	7.525 ±0.005	7.46 ±0.001	7.75 ±0.001
I	6.68	7.35	7.28	7.045	7.71	6.265	7.56		7.115	7.41	7.325	7.245	7.105	7.185	7.155	7.79	7.83	7.32	7.785

	±0.001	±0.006	±0.006	±0.001	±0.014	±0.001	±0.007		±0.001	±0.014	±0.013	±0.01	±0.007	±0.004	±0.001	±0.016	±0.012	±0.012	±0.014
K	6.29	6.955	6.76	6.57	7.205	5.925		7.185	6.735	6.855	6.915	7.015	6.75	6.82	6.835	7.27	7.19	6.915	7.235
	±0.001	±0.002	±0.005	±0.001	±0.001	±0.001		±0.001	±0.001	±0.001	±0.003	±0.009	±0.001	±0.002	±0.001	±0.001	±0.009	±0.01	±0.001
L	6.38	7.01	6.91	6.66	7.345	6.095	7.165	7.33	6.825	7.28	6.96	6.99	6.835	6.85	6.96	7.32	7.48	7.29	7.245
	±0.011	±0.002	±0.009	±0.005	±0.014	±0.006	±0.001	±0.012	±0.001	±0.001	±0.004	±0.001	±0.001	±0.001	±0.001	±0.001	±0.014	±0.0135	±0.001
M	6.465	7.1	7.005	6.86	7.335	6.285	7.03	7.425	6.855	7.025	7.07	7.12		6.905	6.95	7.375	7.48	7.025	7.305
	±0.009	±0.01	±0.009	±0.001	±0.007	±0.008	±0.011	±0.014	±0.001	±0.001	±0.009	±0.001		±0.001	±0.001	±0.001	±0.001	±0.001	±0.001
N	6.785	7.36	7.485	7.125	7.385	6.575	7.685	7.535	7.15	7.24	7.34	7.545	6.855	7.185	7.27	7.48	7.53	7.04	7.83
	±0.016	±0.008	±0.009	±0.013	±0.001	±0.001	±0.002	±0.009	±0.012	±0.001	±0.003	±0.001	±0.001	±0.001	±0.007	±0.002	±0.006	±0.001	±0.015
Q	6.43	7.11	6.965	6.785	7.33	6.225	7.235	7.19	6.855	6.975	7.04	7.115	6.885	6.905	6.935	7.38	7.19	7.035	7.335
	±0.001	±0.008	±0.001	±0.001	±0.012	±0.003	±0.005	±0.015	±0.013	±0.001	±0.011	±0.001	±0.001	±0.001	±0.001	±0.002	±0.014	±0.004	±0.011
R	6.34	6.95	6.785	6.67	7.22	6.235	7.145	7.19	6.795	6.855	6.895	6.49	6.785	6.82	6.86	7.255	7.19	6.905	7.27
	±0.001	±0.007	±0.011	±0.01	±0.001	±0.012	±0.006	±0.001	±0.011	±0.001	±0.001	±0.001	±0.01	±0.001	±0.001	±0.001	±0.001	±0.001	±0.002
S	6.53	7.195	7.34	7.04	7.67	6.135	7.335	7.52	6.96	7	7.05	7.23	6.985	6.955	7.025	7.415	7.34	7.085	7.42
	±0.003	±0.016	±0.011	±0.011	±0.011	±0.008	±0.012	±0.013	±0.01	±0.003	±0.001	±0.013	±0.011	±0.011	±0.008	±0.001	±0.006	±0.001	±0.012
T	6.905	7.47	7.4	7.185	7.8	6.535		7.555	7.22	7.295	7.375	7.5	7.29	7.27	7.4	7.8	7.605	7.425	7.665
	±0.012	±0.004	±0.001	±0.001	±0.012	±0.002		±0.011	±0.001	±0.001	±0.004	±0.011	±0.001	±0.001	±0.001	±0.009	±0.002	±0.001	±0.001
V	6.665	7.085	7.645	6.96	7.555	6.315	7.485	7.605	7.065	7.2	7.22	7.205	7.095	7.085	7.135	7.56	7.61	7.4	7.625
	±0.008	±0.001	±0.01	±0.005	±0.008	±0.009	±0.006	±0.005	±0.004	±0.001	±0.005	±0.009	±0.008	±0.001	±0.005	±0.001	±0.009	±0.012	±0.001
W	6.69	7	7.015	6.78	7.57	6.1	7.115	7.525	6.83	7.215	6.875	7.235	6.75	6.775	6.93	7.295	7.89	6.745	7.41
	±0.011	±0.001	±0.001	±0.001	±0.014	±0.003	±0.001	±0.012	±0.001	±0.011	±0.001	±0.013	±0.001	±0.001	±0.001	±0.001	±0.01	±0.008	±0.001
Y	6.625	7.22	7.19	6.935	7.65	6.22	7.29	7.545	6.91	7.17	7.115	7.35	6.945	6.93	7.1	7.425	7.555	7.125	7.595
	±0.001	±0.003	±0.001	±0.001	±0.012	±0.001	±0.001	±0.012	±0.001	±0.013	±0.001	±0.011	±0.002	±0.001	±0.001	±0.001	±0.016	±0.001	±0.001

Table S4. The average chemical shifts (in ppm) δ_{NH} (upper) and $\delta_{HC\alpha}$ (lower) of each dipeptide. For each dipeptide, there are two N-H^N protons and two C^{α}-H^{α} protons. The average values are given in this table.

	C-terminal amino acid																		
	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	8.3	8.37	8.395	8.39	8.165	8.44	8.41	8.155	8.385	8.28	8.355	8.405	8.37	8.34	8.33	8.245	8.195	8.025	8.125
	4.27	4.4	4.42	4.39	4.4	4.09	4.46	4.21	4.49	4.29	4.36	4.28	4.28	4.28	4.36	4.31	4.21	4.4	4.36
C	8.425	8.495	8.49	8.495	8.265	8.535	8.52	8.33	8.46	8.415	8.49	8.51	8.475	8.475	8.445	8.37	8.325	8.11	8.24
	4.39	4.53	4.6	4.51		4.22		4.34	4.39	4.41	4.49	4.6	4.41	4.4	4.5	4.46	4.34	4.54	4.5
D	8.335	8.49	8.41	8.41	8.16	8.435	8.42	8.265	8.395	8.33	8.4	8.4	8.4	8.38	8.35	8.27	8.235	8.02	8.125
	4.43		4.6	4.44	4.57	4.24		4.42		4.44	4.51	4.63	4.43	4.43	4.52	4.48	4.38	4.55	4.54
E	8.38	8.455	8.465	8.45	8.245	8.51	8.495	8.28	8.415	8.36	8.44	8.485	8.455	8.435	8.415	8.33	8.285	8.12	8.22
	4.27	4.4		4.28	4.37	4.09		4.23	4.27	4.29	4.37	4.47	4.28	4.28	4.37		4.23	4.39	4.37
F	8.275	8.34	8.34	8.315		8.39	8.365	8.12	8.285		8.33	8.34	8.32	8.3	8.285	8.21			8.105
	4.4	4.51		4.4		4.19	4.55	4.31	4.38		4.48	4.57	4.36	4.38	4.49				4.47
G	8.3	8.355	8.375	8.36	8.14	8.385	8.38	8.175	8.32	8.28	8.355	8.385	8.355	8.33	8.33	8.235	8.18	8.005	8.105
	4.12	4.26	4.28	4.13	4.21	3.94	4.3	4.06	4.12	4.12	4.2	4.33	4.13	4.13			4.05	4.22	4.18
H	8.435	8.495	8.495	8.515	8.28	8.54		8.345	8.46	8.42	8.49	8.52	8.5	8.47	8.445	8.365	8.35	8.13	8.255
	4.5	4.55	4.63	4.48	4.61	4.31	4.65	4.39	4.47	4.49	4.57	4.68	4.49	4.48	4.59	4.28	4.38	4.61	4.58
I	8.255	8.325	8.32	8.325	8.12	8.395	8.18		8.285	8.18	8.305	8.35	8.325	8.305	8.27	8.175	8.135	7.98	8.075
	4.22	4.33		4.23	4.34	4.02			4.21	4.21	4.32	4.41	4.22	4.22	4.31		4.1		4.32
K	8.32	8.39	8.4	8.415	8.195	8.455		8.235	8.35	8.295	8.38	8.425	8.395	8.365	8.34	8.255	8.235	8.065	8.17
	4.28	4.4	4.42	4.27	4.5			4.22	4.28	4.3	4.37		4.29	4.29	4.37		4.2	4.4	4.36

L	8.28	8.35	8.385	8.37	8.14	8.435	8.405	8.155	8.305	8.25	8.34	8.405	8.35	8.325	8.305	8.215	8.145	8.01	8.115
	4.28	4.4	4.42		4.4	4.09		4.23	4.29	4.31	4.38	4.47	4.3	4.3	4.38		4.2		4.37
M	8.355	8.43	8.445	8.425	8.23	8.495	8.47	8.25	8.39	8.335	8.415	8.465		8.4	8.375	8.295	8.25	8.08	8.2
	4.36	4.48		4.37	4.48			4.31	4.36	4.38	4.46	4.55		4.37	4.45	4.42	4.31		4.44
N	8.39	8.455	8.46	8.47	8.2	8.5	8.48	8.285	8.425	8.385	8.455	8.465	8.43	8.44	8.405	8.325	8.285	8.08	8.16
	4.49	4.61		4.48		4.3		4.44	4.47	4.49	4.58	4.49	4.37	4.48			4.42		4.58
Q	8.37	8.435	8.445	8.45	8.22	8.49	8.475	8.225	8.405	8.35	8.425	8.465	8.445	8.415	8.39	8.31	8.225	8.1	8.205
	4.29	4.42	4.44		4.39	4.1		4.22	4.29	4.31			4.3	4.3	4.39		4.2	4.41	4.37
R	8.345	8.41	8.415	8.44	8.22	8.465	8.455	8.25	8.37	8.32	8.4	8.445	8.415	8.385	8.36	8.275	8.255	8.09	8.2
	4.29	4.41	4.43	4.27	4.41			4.23	4.29	4.31	4.38	4.48	4.3	4.3	4.39		4.22		4.38
S	8.375	8.43	8.455	8.45	8.205	8.465	8.47	8.245	8.405	8.355	8.425	8.465	8.44	8.415	8.395	8.305	8.255	8.055	8.175
	4.37	4.51	4.52	4.37	4.36	4.14		4.32	4.37	4.38	4.46		4.38	4.38	4.47	4.43	4.32	4.49	4.47
T	8.285	8.335	8.37	8.365	8.155	8.405		8.2	8.32	8.28	8.35	8.39	8.355	8.335	8.3	8.22	8.22	8.02	8.135
		4.44	4.46		4.42				4.31	4.32	4.4	4.5	4.32	4.32		4.38		4.42	4.38
V	8.26	8.325	8.325	8.33	8.115	8.395	8.38	8.14	8.295	8.235	8.315	8.355	8.33	8.305	8.275	8.2	8.16	8.01	8.115
	4.19	4.32	4.35	4.19		4		4.09	4.18	4.21	4.28		4.2	4.2	4.29	4.25	4.08		4.28
W	8.13	8.185	8.2	8.155	7.94	8.275	8.21	7.98	8.13	8.115	8.155	8.2	8.145	8.12	8.125	8.07	7.995	7.53	7.88
	4.37	4.47	4.47	4.35	4.48	4.66	4.5	4.5	4.34	4.4	4.42	4.54	4.33	4.49	4.44			4.42	4.45
Y	8.24	8.295	8.305	8.295	8.09	8.36	8.32	8.085	8.255	8.21	8.3	8.31	8.285	8.265	8.25	8.185	8.1	7.875	8.06
	4.37	4.47	4.53	4.36	4.47		4.51	4.28	4.33	4.37	4.44	4.54	4.35	4.34	4.45		4.26	4.46	4.44

Table S5. The characteristic features of the experimentally measured temperature-dependent CD spectra of all the dipeptides (Ac-Gly-Gly-NH_2 excluded). Depending on the existence of a single isodichroic point in the wavelength range from 190 to 220 nm, we add the symbol “O” or “X”. In the case that there exist two isodichroic points in the temperature-dependent CD spectra, the symbol “OO” is used. The number in the second line is the wavelength of the isodichroic point. The number in the third line is the wavelength of the negative peak and its CD intensity at 20°C is given in the fourth line. In the cases that the negative peak wavelengths and the corresponding CD intensities are not determined, we add “X” and “x” in the third and fourth lines. They are the dipeptides containing aromatic side chains, because their CD spectra are largely dictated by the contributions from the aromatic side chains. To help the readers to understand the following table, let us consider the AC dipeptide (Ac-Ala-Cys-NH_2) as an example. Its temperature-dependent CD spectra exhibit a single isodichroic point at 200 nm. The negative peak is at 193 nm and its CD intensity is -92 in unit given in Fig.S1.

	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**P**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	O 202 193.1 -236	O 200 193 -92	O 204 196 -175	O 201 194 -33.6	X	X	X X 196.5 -94.2	O 200 192.8 -173	O 201.4 192.5 - 126.7	O 201 193.3 -194	O 201 193 -151	O 203.4 195 -191	O 203 191 -165	O 201 193.4 -139	O 201 191 -88	O 202 193 -118	O 193 -116	O 200 192 -93.3	O 202 196 -60	O 197 X X
C	X X 195 -60	O 200 196 -8	O 207 198 - 153.3	O 206 196 -105	X	O 203 193 -22	X	O 203 194 -90	O 204 193 -102	O 204 193 -44	O 204 194 -152	O 203.2 195 -27.7	X	O 204.3 195 -91	O 204.7 192.4 -42	O 205.4 194.7 - 128.5	O 203.2 194.5 - 109.6	O 201.2 193.6 125.5	O 206 200 -141	X

D	O 202 194 -302	X	O 204 196 -151	O 202 194 -124	X	O 199 197 -51.6	X	O 199 193 -99	O 201 193.1 138.8	O 201.7 193 -250	O 201 193 -155	O 202.8 195.7 130.3	O 203 192 -203	O 201.3 193.6 - 131.6	O 202 192 -75	O 202 194 -205	O 201 194 -166	O 200 193 -129	O 207 196 -217	X
E	O 202 193 -180	O 200 194 -112	O 203 196 -168	O 202 195 -169	X	X	X	O 200 193 -140	O 203 195 -155	O 202 193.4 -164	O 201.6 194 - 152.8	O 203 196.2 - 110.7	O 203 190 - 101.7	O 201 194 - 112.6	O 202 191.8 -79	O 202.4 194.5 - 110.3	O 200.5 194 - 127.6	O 200.7 193 - 159.3	O 207 198 -175	X
F	O 205 X X	X	X	O 204 X X	OO 205.7 218	X	X	X	O 205 X X	X	O 204.7 X x	O 203.4 X x	X	O 204.7 X x	O 205.2 X x	O 204.5 X x	O 203.6 X x	X	X	X
G	O 206 192 -128	O 210 194 -47	O 207 195 -95	O 205 194 -100	X	X	X	O 209 194 -62.7	O 206 192 -82.6	O 203.3 192 -130	O 203.3 192 - 109.2	O 208.8 194.5 - 111.5	O 214.6 194.3 - 130.5	O 204 192 -56.7	O 205.6 190 -60	O 209.3 194 -72	O 210 194 -86	O 210 193.7 -67	O 206 197 -67.8	O 195 X X
H	O 202 X X	X	O 205 X X	O 205 X X	X	X	X	X	X X 192 -91	O 203 193.7 - 103.1	O 202 192.8 -83.1	O 206 X x	O O 200.9 224.2	X	O 202.4 X x	X	X	O 205.3 193.5 -53.8	X X 198 -106	O 207 X X

I	O 204 194 -151	O 201 195 -74	O 205 197 -151	O 203 196 -184	X	X	X	X	O 203 194 -83.7	O 203 195 -208	O 203.3 194.5 - 185.2	O 207.5 197 -76.4	O 212.6 188 -4.5	O 202.6 194.8 - 138.2	O 203.7 193.5 -51.7	O 205 195.4 -164	O 201.5 195 - 140.6	X	O 210 198 -172	X
K	O 202 193 -154	O 200 194 -77	O 204 196 -102	O 203 195.7 -120	O 198 X X	X	X	O 200.7 193 -113	O 202 193 -111	O 202 193 -146	O 201.8 193.7 -63.2	O 204 196 -67.6	O 202.5 191.4 - 106.5	O 201 193.7 - 103.4	O 202 193 -78	O 202 194.5 - 158.5	O 200.6 194 -116	O 201 193 - 142.5	O 205.8 198 - 132.3	O 197 191 160.2
L	O 202 193 -122	O 200 194 -137	O 203 196 -217	O 202 195 - 128.4	X	X	X	X	O 201.6 193 -87	O 202 194 -187	O 201.6 194 -162	O 203 195 -116	O 202 190 -226	O 201 193 - 157.2	O 201.4 193 -98.2	O 202 194 169	O 201 194 - 193.6	O 200.5 193 - 176.7	O 206 197 - 146.5	O 198 X X
M	O 202 193.6 -141	O 201 194.5 -101	O 203 196.7 -170	O 202.4 195.4 - 124.5	X	X	X	O 200 193 -68	O 201.7 193 -130	O 202 193 -160	O 201.6 193 -101	O 202 196 -93.5	O 202 191 -108	O 201 195 - 103.8	O 202 192 -63.3	O 202 194 - 118.3	O 200 194 - 108.3	O 200.6 193 -86.4	O 207 198 -145	O 198.5 X X
N	O 203 194 -156	O 200 194.5 -	O 205 196.6 -	O 203 196 -171	O 199.7 X X	O 200.4 195 -75.5	X	O 200 194 -86	O 203 193.6 -104	O 202.2 193 -118	O 202.6 193 -	O 206.4 196 -	X	O 201.3 194 -80.7	O 202 193 -	O 203 194 -	O 203 194 -	O 201 194 -164	X	O 215.5 198 -

		106.2	187.3								113.8	131.6			107.5	148.4	232.4		102.3
P	O 208.6 197 -120	X X 202 -84	O 210 201 -163	O 208 200 -116	O 205.6 X X	O 201 X x	X	O 207 198 -157	O 207 198 -132	O 207 198 -142	O 207 199 -127	O 211 200 - 104.3	O 209 197 -283	O 207.8 201 -94.7	O 208 201 -49.6	O 209 199 - 143.3	O 207.6 199 -90.7	O 207 198 - 120.7	X X 202 - 151.6	X
Q	O 203 194 - 135.7	O 200.5 194.3 - 104.7	O 203.8 197 - 125.3	O 203 195 - 168.3	X	O 194 X X	O 192 197 -56.5	O 201 193 -118	O 201 193 -78.6	O 202.4 193 - 132.5	O 201.6 193.4 -87.5	O 203.6 196 -92.5	X X 191 -88.4	O 201.4 194 -88	O 202 193 -86	O 202.5 194.5 - 128.2	O 200 194 - 105.5	O 200.7 193 - 130.6	O 206 199 -123	O 197.5 X X
R	O 202.6 191.6 -65.4	O 200.5 X X	O 207.4 198 - 148.5	X X 196 109.8	O 199 X X	X	X	O 201 191 -66.2	O 202 191 -77.6	O 202 192 -76	O 202.6 193 -145	O 204 196 -82	X X 189 -87	O 201 X X	X	O 202 193 -67	O 202 194 -78.4	O 201 193 -73	O 216 200 -114	O 199 X X
S	O 206 194 -260	O 201 194 -24	O 207 196 -162	O 203.7 195.8 -63.4	O 198 X X	O 203 195 -95	X	O 201 194 -163	O 203 193 -71	O 202 192 -65	O 203 193 - 209.8	O 206 195 -81	X X 191 - 143.4	O 201 194 -77.8	O 204.7 192 -189	O 204.4 194 -88	O 204 194 -46.8	O 201 193 -167	O 206.8 197 -167	O 198 X X

T	O 205 194 -92.7	O 203 195 -95	O 208 197 -124	O 206 195 -92.8	X	X X 196.4 -37.5	O 192.8 X x	O 202 194 -113	O 204.5 194.3 -98.9	O 204 194 -169	O 203.3 194.1 170.3	O 210 196 -139	X	O 203 199.5 -100	O 204 193.3 -72.3	O 206 195 -120	O 202 194 -130	O 202 194 -165	X X 198 - 137.7	O 199.8 192 -94
V	O 204 194 -231	O 201 194 - 111.6	O 204 197 - 158.7	O 203.6 195 - 141.8	O 200 186 -134	X	O 192.4 X x	O 201 193 -191	O 202.6 193.5 -42.7	O 203 194 -190	O 203.7 194 -212	O 207 197 -196	X X 191 -91	O 202 193 -133	O 203 192 -55	O 203.7 195 -87.8	O 201 194 -39	O 201 193 -99	O 205 197 -153	X
W	X X 195 -107	X	O 205.2 199.5 -91.3	X X 198 -116	X	X	X	X X 194 -38	O 203 194 -54	O 202 193 -84	O 199.7 192 -60.7	X	O 213.8 197 -28.7	X	X	O 202.6 195 -54.3	O 202.5 193.7 -35.3	O 204 192 - 105.7	O 217 224 - 252.2	X
Y	O 206 X X	X	O 211.4 X X	O 206 190.5 -73	OO 205.5	X	X	X	O 207 193 -87.5	O 207 193 - 119.7	O 205.6 192 - 111.1	O 209.6 X X	O 211 190 -78.6	O 207 X X	O 207 X X	O 207 191 -73.6	O 206 193 -117	O 207 192 -40.5	O 218	O 198.7 X X

Table S6. Relative P_{II} populations (at 25 °C) of dipeptides, denoted as $P_{P_{II}}(X_1, X_2)$, obtained from the NMR coupling constants are in the first row. In the cases of the GX and XG dipeptides, the P_{II} population given in this table corresponds to that of the X peptide. In the second row, ΔH (in kcal/mol) values associated with the $P_{II} \rightarrow \beta$-strand conformational transitions are given. In the third row, $T\Delta S$ (at 300 K) values in kcal/mol associated with the $P_{II} \rightarrow \beta$-strand conformational transitions are given. In cases of F, W and Y, we couldn't obtain ΔH and ΔS because their CD spectra are dictated by the contribution from aromatic side-chain.

	C-terminal amino acid																		
	A	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**K**	**L**	**M**	**N**	**Q**	**R**	**S**	**T**	**V**	**W**	**Y**
A	0.78	0.62	0.73	0.61	0.65	0.86	0.66	0.57	0.53	0.66	0.72	0.77	0.77	0.78	0.65	0.68	0.7	0.71	0.61
	4.93	2.97	3.61	2.96				3.85	2.99	3.71	4.44	3.13	4.73	4.23	3.71	3.93	4.48		
	4.2	2.69	3.04	2.72				3.7	2.95	3.34	3.92	2.43	4.03	3.5	3.36	3.52	4		
C	0.73	0.67	0.67	0.64	0.54	0.74	0.58	0.51	0.67	0.62	0.66	0.7	0.71	0.72	0.63	0.6	0.61	0.64	0.53
	5.81	2.47	2.17	3.9				3.83	4.12	3.48	4.53	4.48	5.12	6.43	3.43	3.47	3.98		
	5.26	2.06	1.77	3.59				3.85	3.73	3.21	4.17	4.03	4.62	5.92	3.15	3.25	3.74		
D	0.71	0.66	0.62	0.64	0.53	0.72	0.64	0.56	0.62	0.64	0.65	0.67	0.7	0.7	0.62	0.6	0.65	0.6	0.51
	3.64		1.9	3.29						3.32	3.15	2.17	3.61	4.31	2.61	2.93	3.34		
	3.13		1.62	2.99						3.01	3.08	1.77	3.13	3.85	2.33	2.7	3		
E	0.74	0.66	0.67	0.7	0.57	0.79	0.58	0.59	0.71	0.67	0.68	0.72	0.74	0.73	0.66	0.61	0.63	0.66	0.57
	4.88	3.5	2.63	5.03				4.37	4.61	4.33	4.92	2.72	5.59	5.78	4.11	4.01	4.52		
	4.31	3.13	2.36	4.56				4.17	4.11	3.96	4.5	2.18	5.02	5.23	3.74	3.76	4.23		
F	0.57	0.58	0.6	0.63		0.7	0.55	0.5	0.63		0.61	0.61	0.67	0.66	0.57	0.57			0.46
G	0.69	0.57	0.58	0.63	0.51		0.4	0.48	0.58	0.53	0.57	0.59	0.65	0.61	0.48	0.46	0.58	0.61	0.51
	4.13	4.6	3.02	4.05				5.15	4.64	4.04	3.29			12.7	4.27	3.77	4.43		

	3.67	4.44	2.83	3.74				5.21	4.48	3.89	3.04			12.5	4.21	3.86	4.27		
H	0.65	0.59	0.59	0.61	0.46	0.52		0.51	0.58	0.54	0.57	0.58	0.64	0.48	0.52	0.51	0.56	0.53	0.45
										2.05	2.2			3.09					
										1.97	2.05			3.16					
I	0.67	0.59	0.59	0.63	0.47	0.71	0.5		0.6	0.53	0.58	0.67	0.66	0.62	0.57	0.48	0.49	0.57	0.45
	4.05	3.34	2.07	3.68					4.42		3.85	2.38	4.67	5.39	3.6				
	3.66	3.15	1.87	3.38					4.22		3.69	1.99	4.31	5.13	3.46				
K	0.73	0.66	0.69	0.71	0.57	0.74		0.58	0.66	0.64	0.65	0.7	0.72	0.69	0.63	0.59	0.63	0.64	0.56
	5	3.7	2.66	4.62				4.55	4.98	4.44	4.38	2.74	-9.61	6.07	4.74	4.12	4.83		
	4.46	3.33	2.2	4				4.39	4.63	4.12	4.03	2.25	-10	5.65	4.45	3.93	4.57		
L	0.73	0.66	0.67	0.71	0.54	0.8	0.58	0.55	0.65	0.55	0.66	0.73	0.72	0.7	0.61	0.59	0.56	0.56	0.55
	4.21	3.55	2.81	4.19					4.16	3.42	4.04	2.92	4.63	5.14	3.66	3.4	3.87		
	3.67	3.17	2.41	3.69					3.83	3.32	3.69	2.35	4.11	4.68	3.44	3.21	3.77		
M	0.73	0.67	0.67	0.69	0.57	0.77	0.65	0.55	0.67	0.64	0.66	0.72		0.71	0.64	0.6	0.59	0.65	0.57
	5.69	4.05	3.23	4.83				5.11	5.21	4.42	4.78	3.43		6.37	5.17	4.73			
	5.13	3.66	2.83	4.4				5.02	4.83	4.12	4.43	2.9		5.89	4.87	4.52			
N	0.73	0.66	0.65	0.69	0.62	0.77	0.53	0.58	0.66	0.65	0.65	0.68	0.83	0.71	0.62	0.64	0.64	0.72	0.49
	3.45	2.34	1.78	3.01		2.04		2.92	3.53	3.28	3.52	1.75	-19.8	3.26	2.71	2.75	2.96		
	2.89	1.96	1.43	2.55		1.33		2.74	3.15	2.94	3.17	1.33	-21	2.74	2.44	2.42	2.63		
Q	0.76	0.69	0.71	0.73	0.6	0.83	0.63	0.59	0.7	0.68	0.69	0.75	0.76	0.74	0.67	0.63	0.69	0.68	0.59
	5.35	3.82	-3.51	-7.88			-3.38	-5.6-	-9.23	-5.55	-7.62	-3.05	-13.6	6.3	-6.56				
	4.69	3.36	-4.1	-8.5			-3.3	-5.8	-9.8	-6	-8.1	-3.7	-14	5.73	-7				
R	0.77	0.72	0.74	0.74	0.61	0.83	0.63	0.62	0.69	0.69	0.71	0.93	0.77	0.74	0.68	0.64	0.67	0.69	0.58
	6.89	4.3	3.15	5.54				5.09	6.51	5.16	5.72	2.59	-17.9		7.11	3.66	6.04		

	6.22	3.77	2.54	4.95				4.84	6.07	4.71	5.23	1.63	-19		6.72	3.33	5.65		
S	0.68	0.59	0.54	0.59	0.44	0.65	0.51	0.47	0.6	0.59	0.61	0.63	0.66	0.65	0.56	0.54	0.57	0.59	0.49
	3.78	2.25	2.18	2.96		1.88		3.38	3.6	2.99	3.99	2.02	3.11	4.43	2.81	3.18	3.48		
	3.37	2.04	2.11	2.76		1.54		3.47	3.38	2.79	3.75	1.71	2.75	4.11	2.68	3.11	3.34		
T	0.66	0.6	0.6	0.63	0.48	0.66		0.54	0.61	0.59	0.6	0.64	0.66	0.64	0.54	0.51	0.58	0.58	0.5
	3.41	2.03	1.87	-3.82				3.3	3.47	3.23	3.37		-4.28	3.86	2.77	2.8	3.41		
	3.04	1.81	1.65	-4.2				3.22	3.24	3.03	3.14		-4.7	3.55	2.69	2.8	3.25		
V	0.72	0.65	0.69	0.7	0.55	0.82	0.57	0.54	0.66	0.63	0.66	0.74	0.72	0.7	0.63	0.59	0.59	0.6	0.53
	4.54		2.23	-4.38			2.8	-2.5	4.67	3.63	4.28	2.52	4.26		3.78	3.62	4.13		
	4.01		1.76	-4.9			2.84	-2.6	4.32	3.34	3.93	1.92	3.73		3.49	3.42	3.94		
W	0.67	0.68	0.65	0.69	0.51	0.81	0.62	0.52	0.66	0.58	0.69	0.67	0.75	0.73	0.63	0.61	0.48	0.71	0.54
Y	0.66	0.61	0.6	0.64	0.48	0.71	0.56	0.5	0.63	0.57	0.61	0.61	0.68	0.66	0.57	0.56	0.54	0.6	0.48

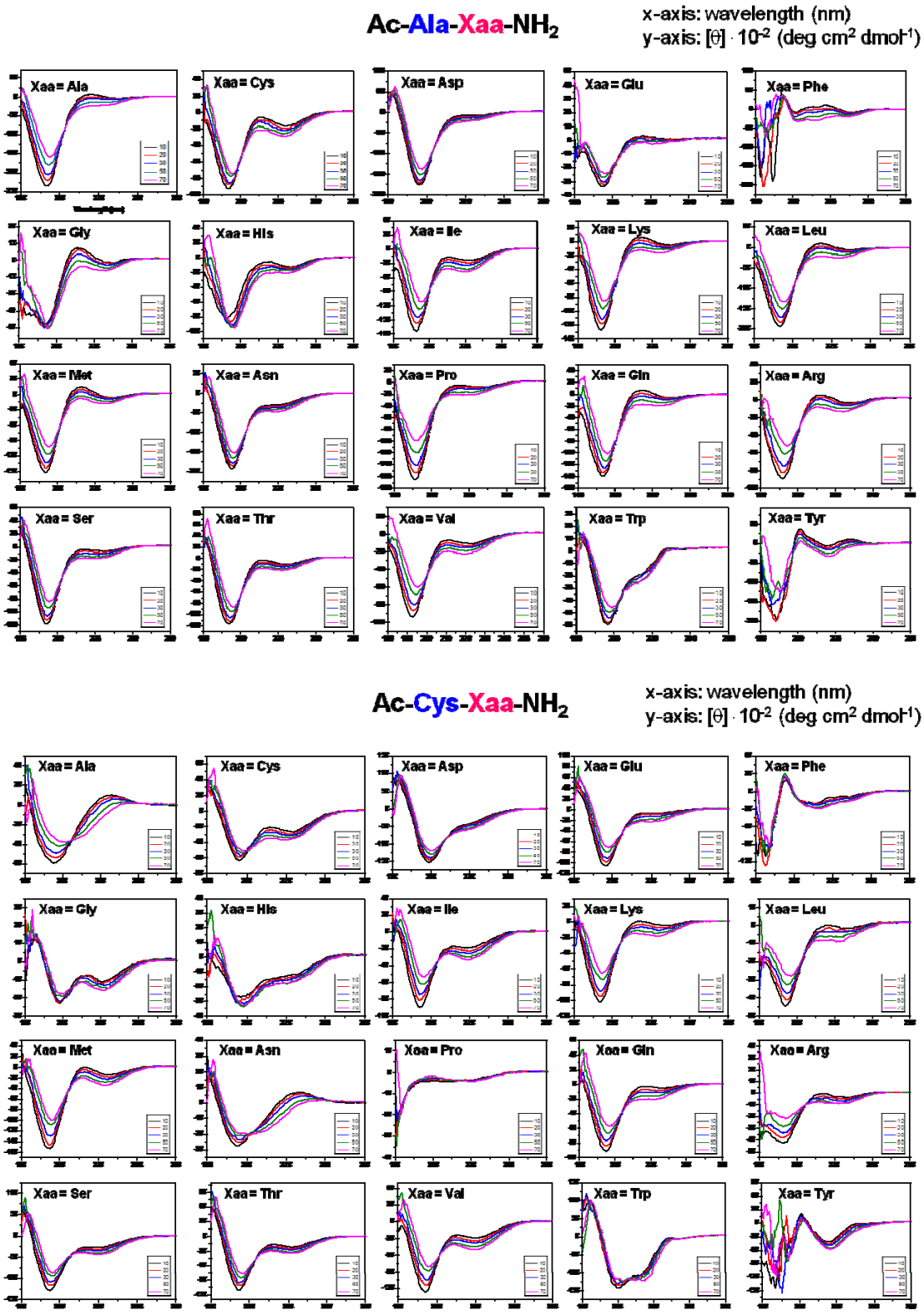

Figure S1: The temperature-dependent CD spectra. Temperatures are 10, 20, 30, 50, 70 °C. The x-axis is the wavelength in nm, and the y-axis is the CD intensity (in 10^2 deg cm^2 dmol^{-1}). To be continued.

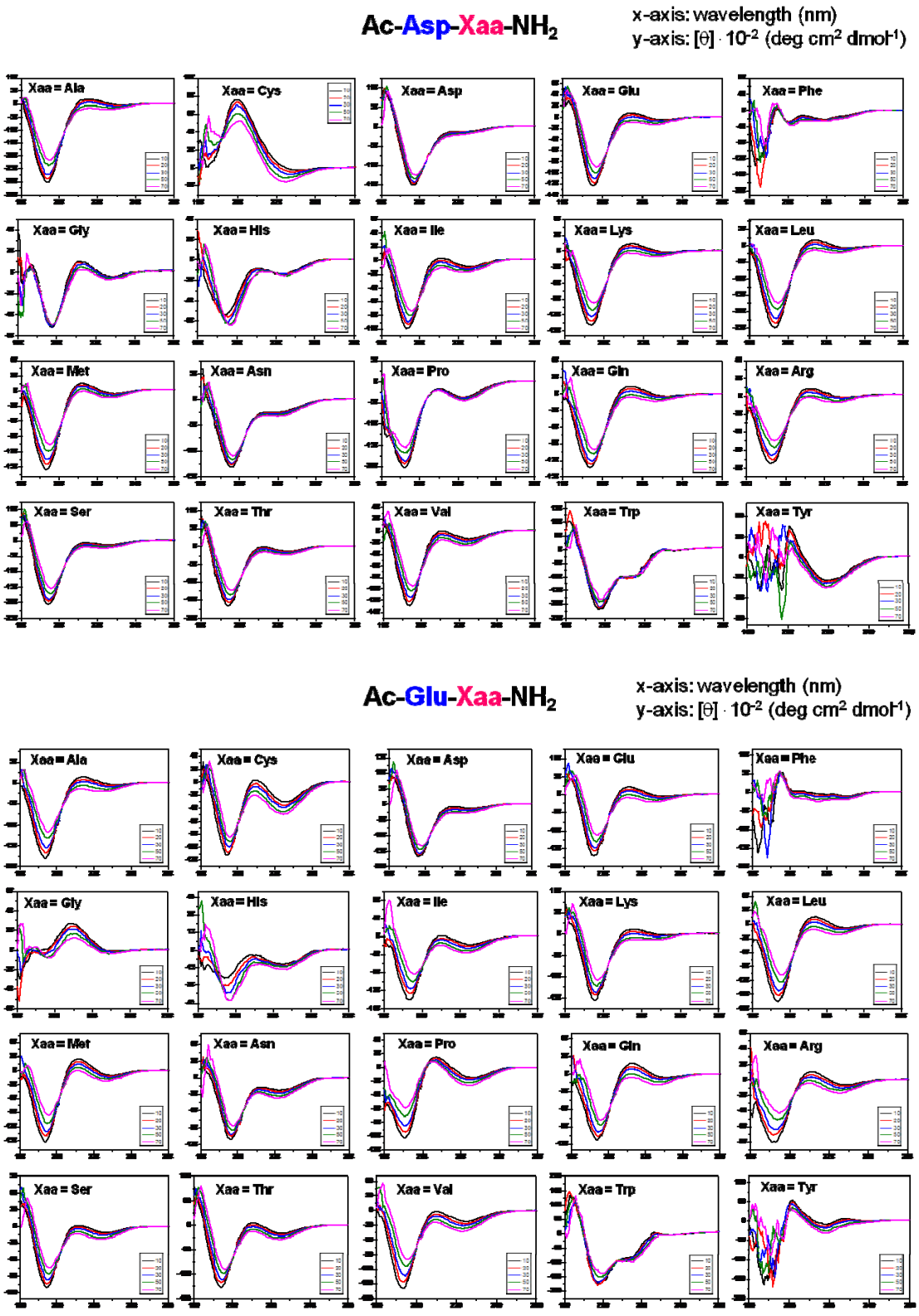

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

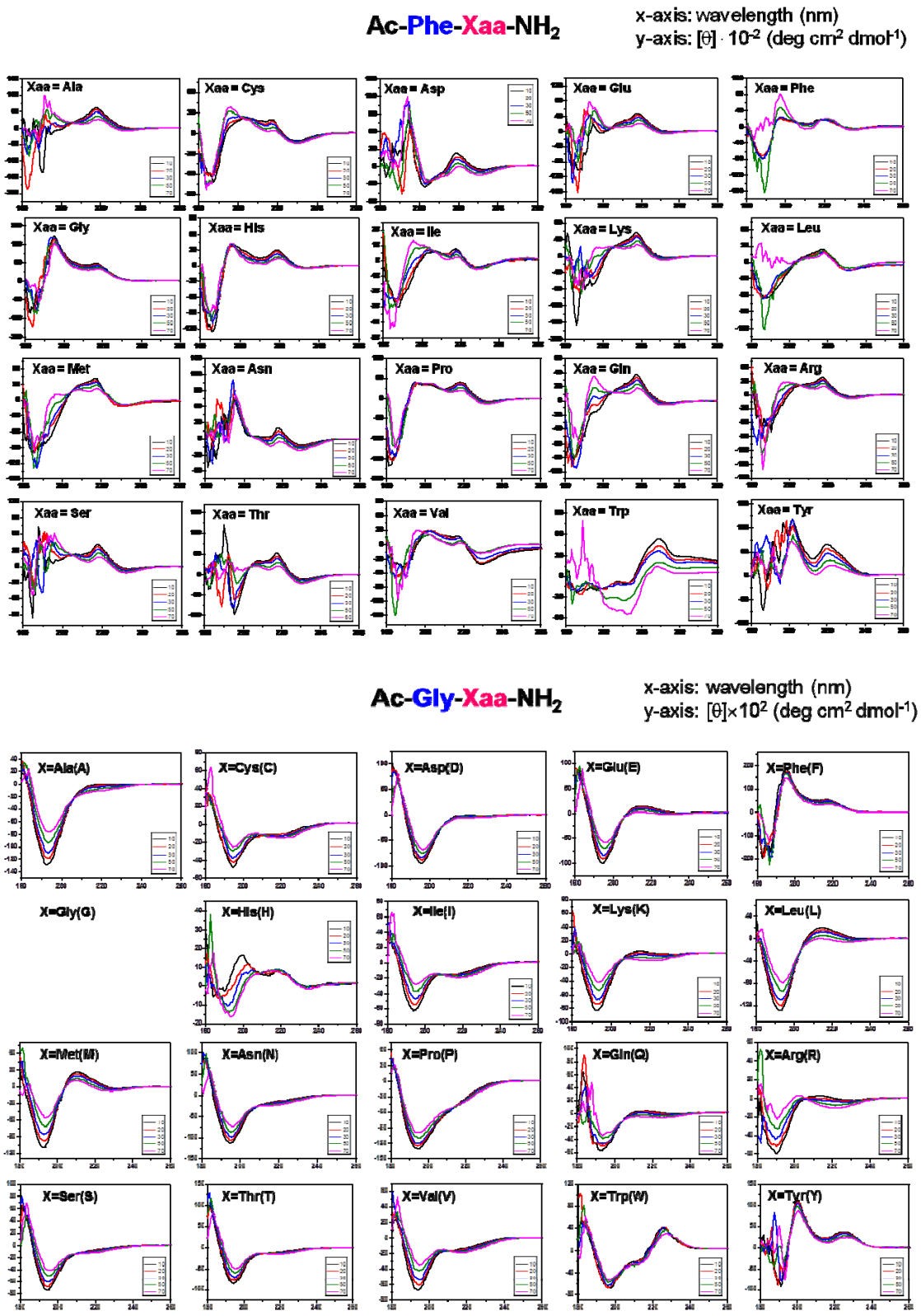

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

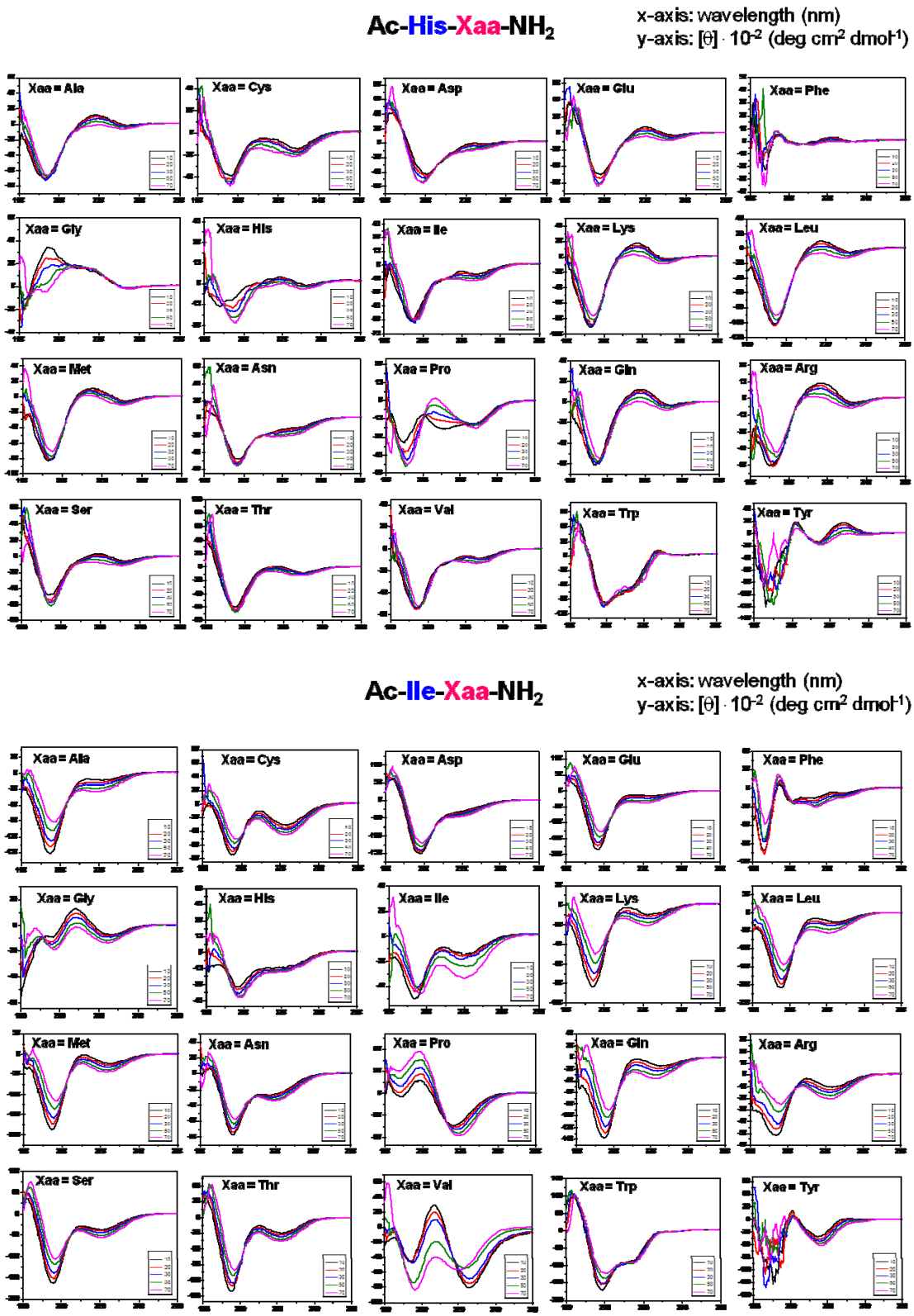

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

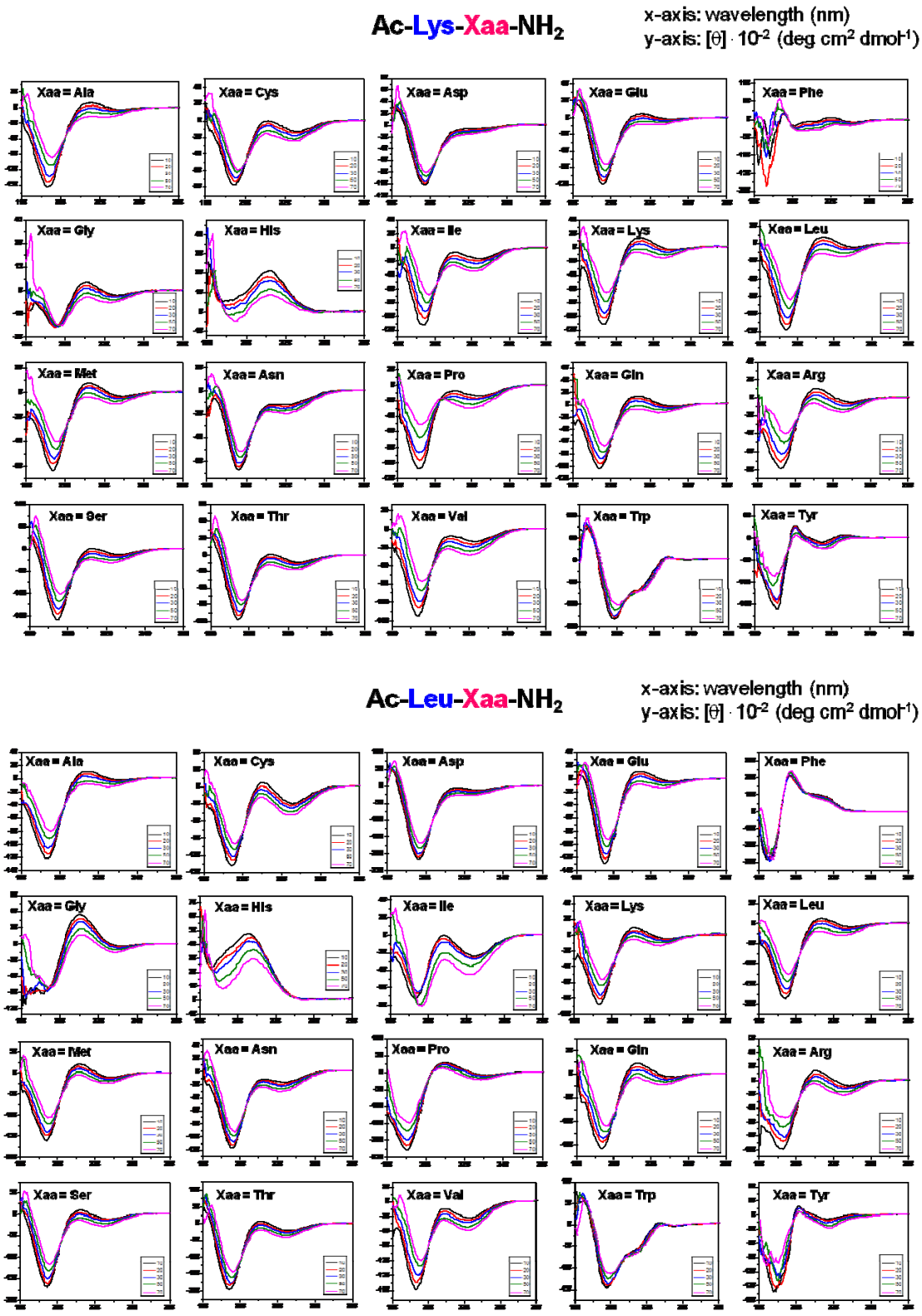

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

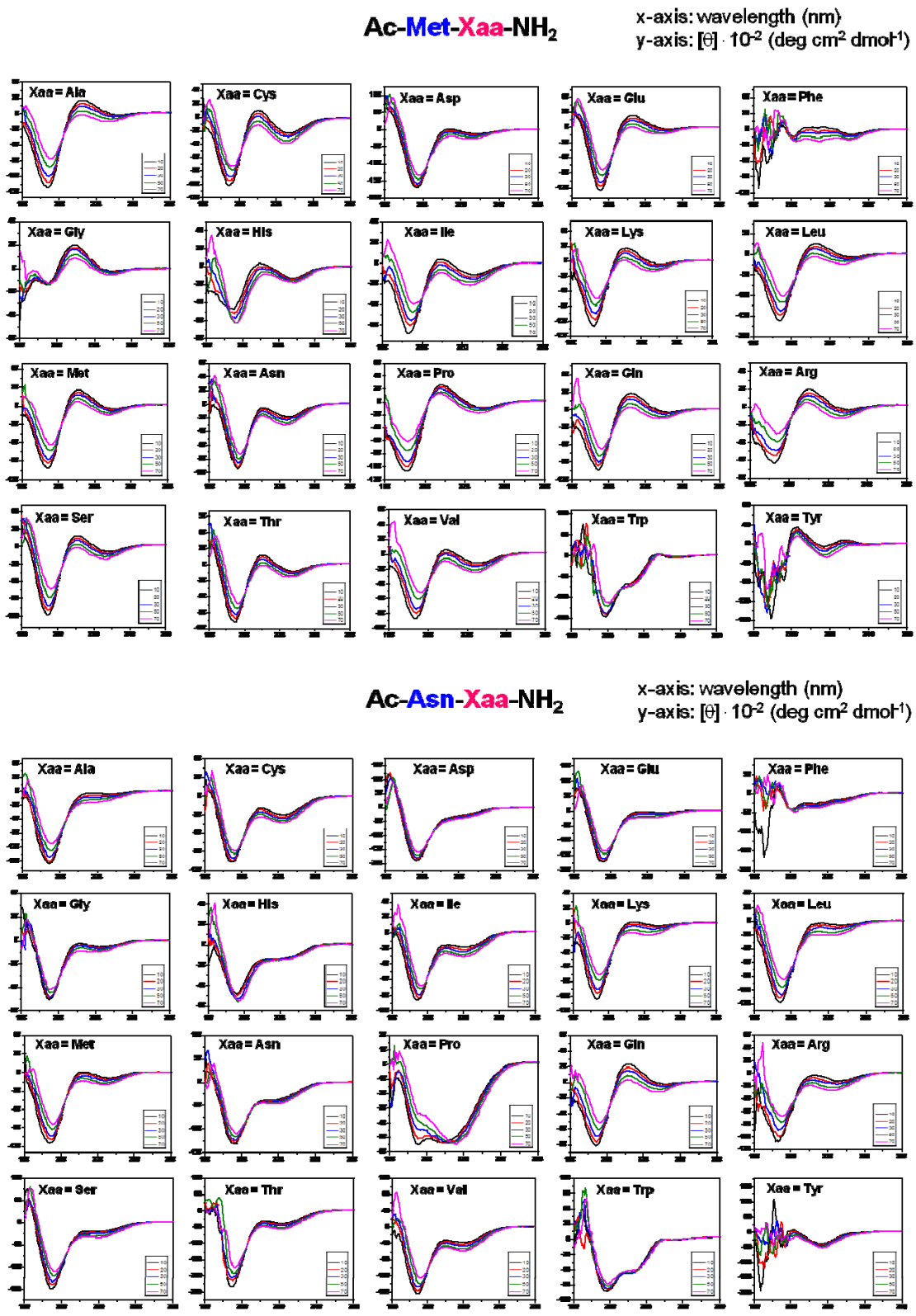

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

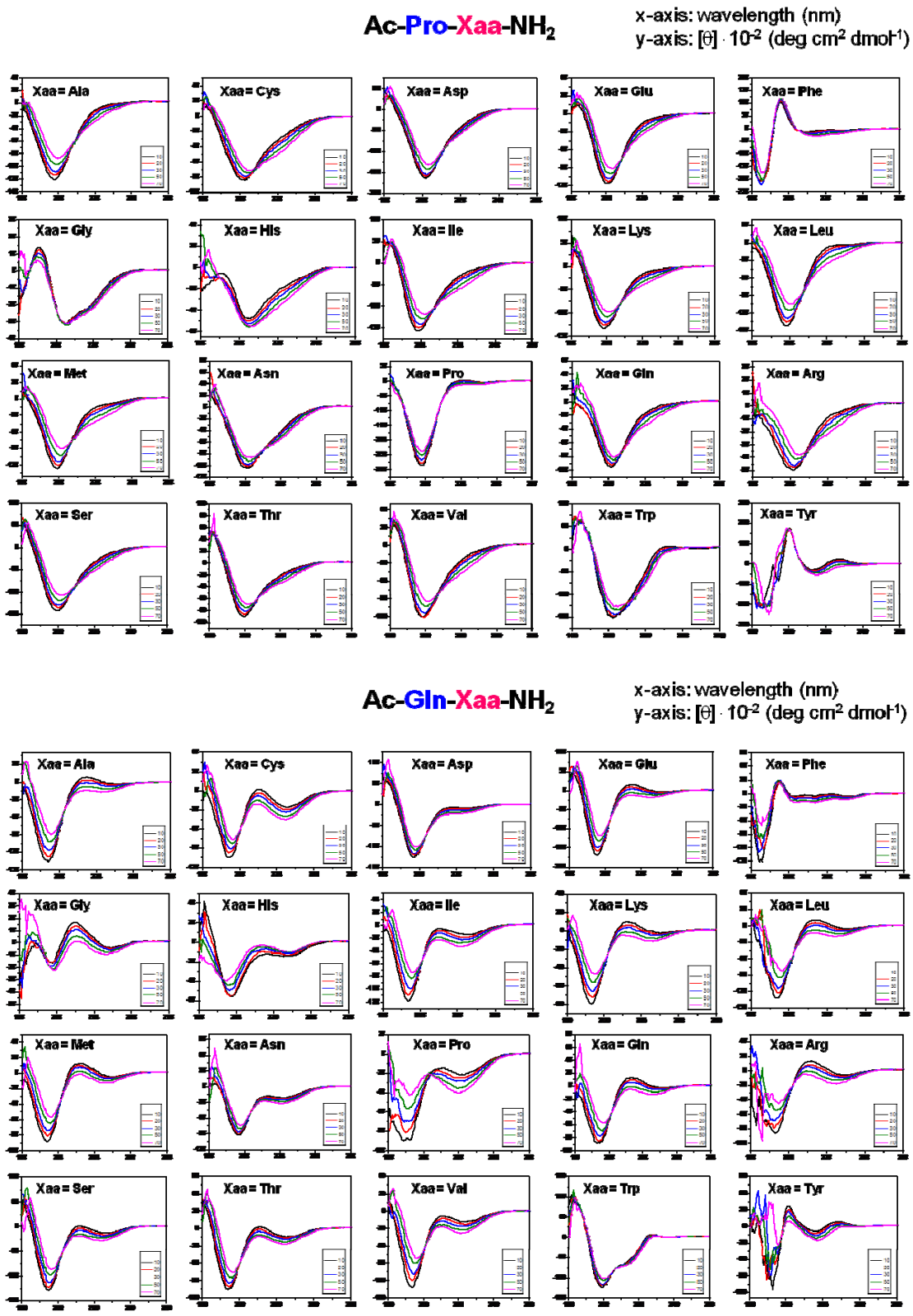

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

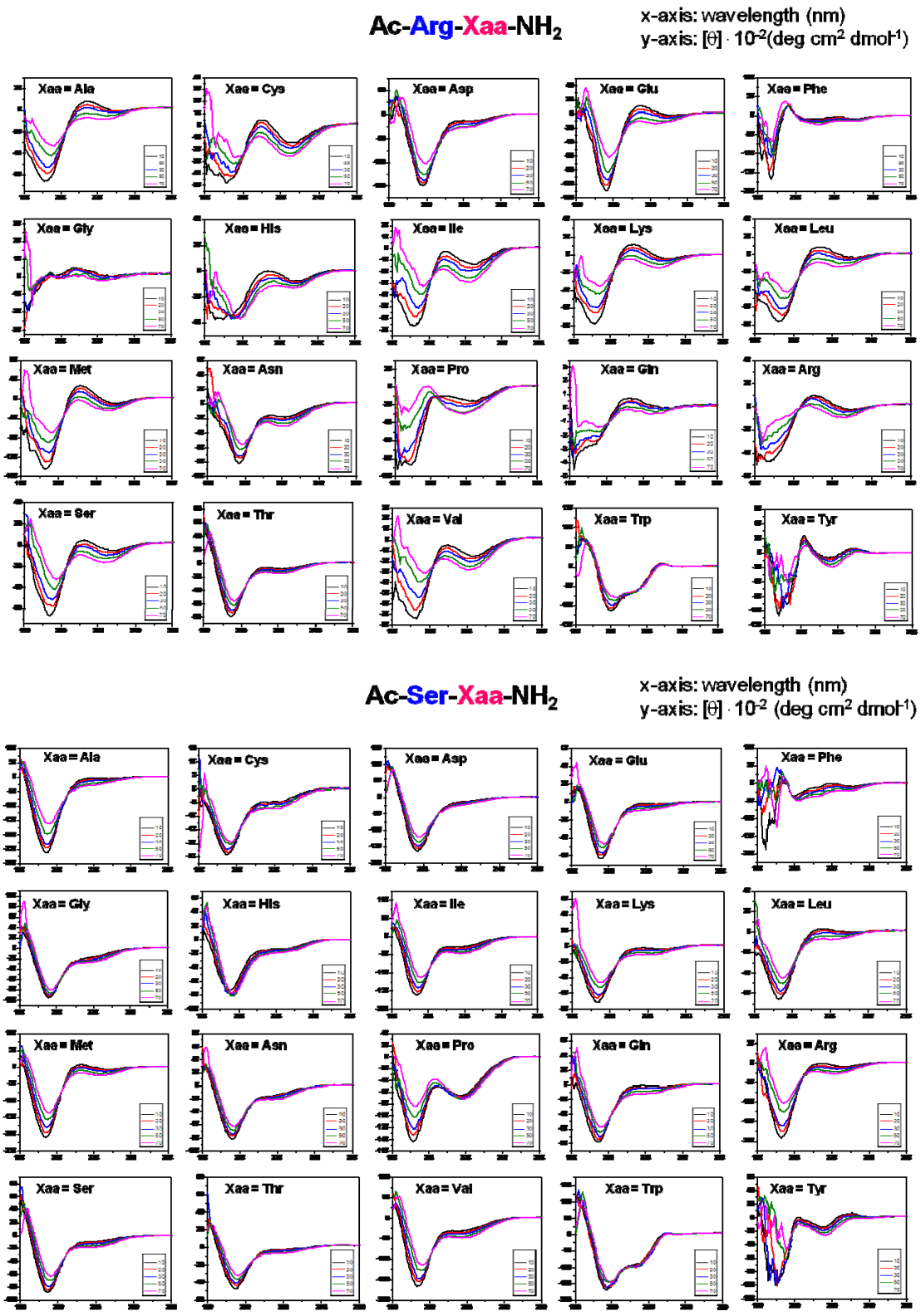

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

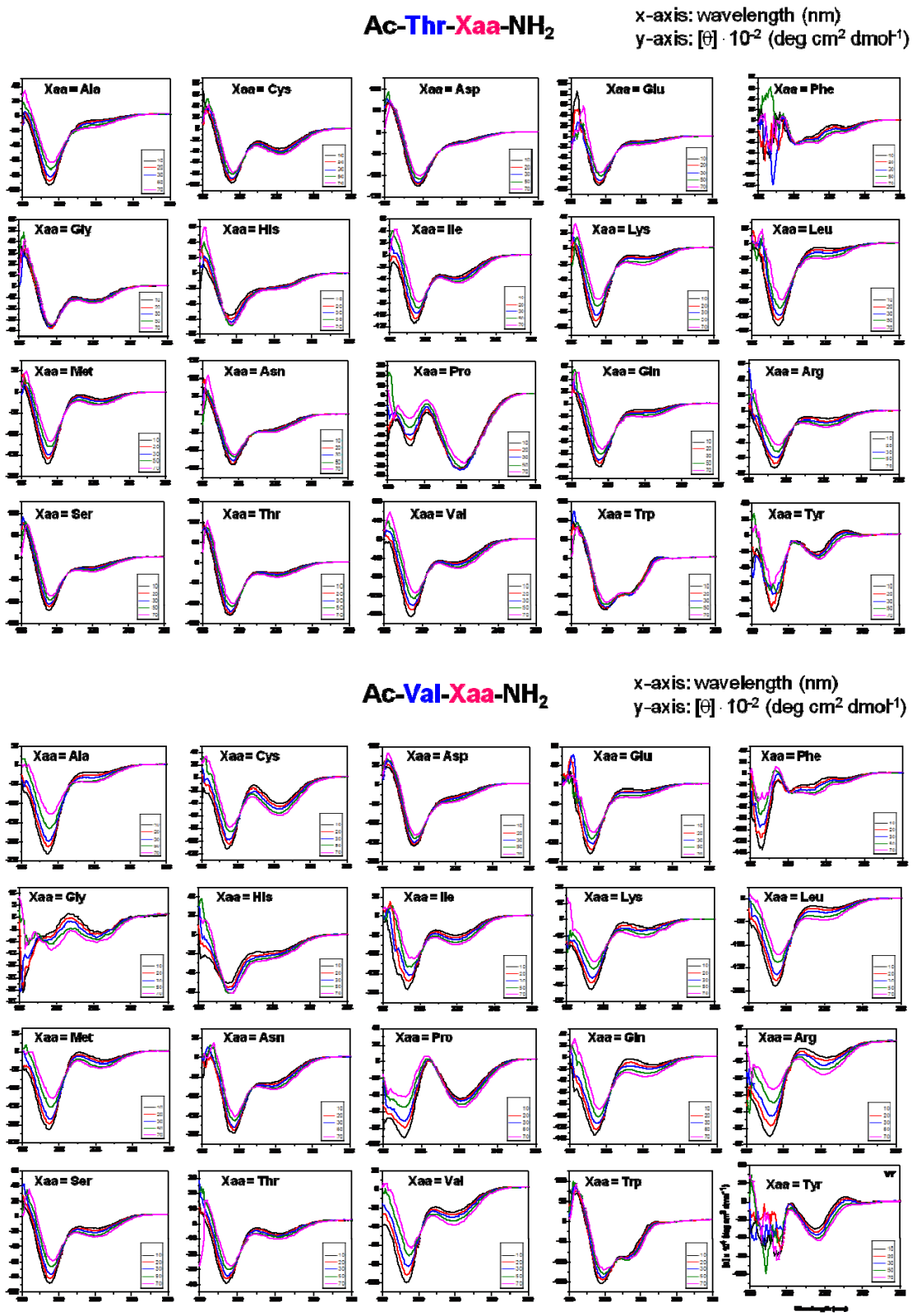

Figure S1: The temperature-dependent CD spectra of dipeptides. To be continued.

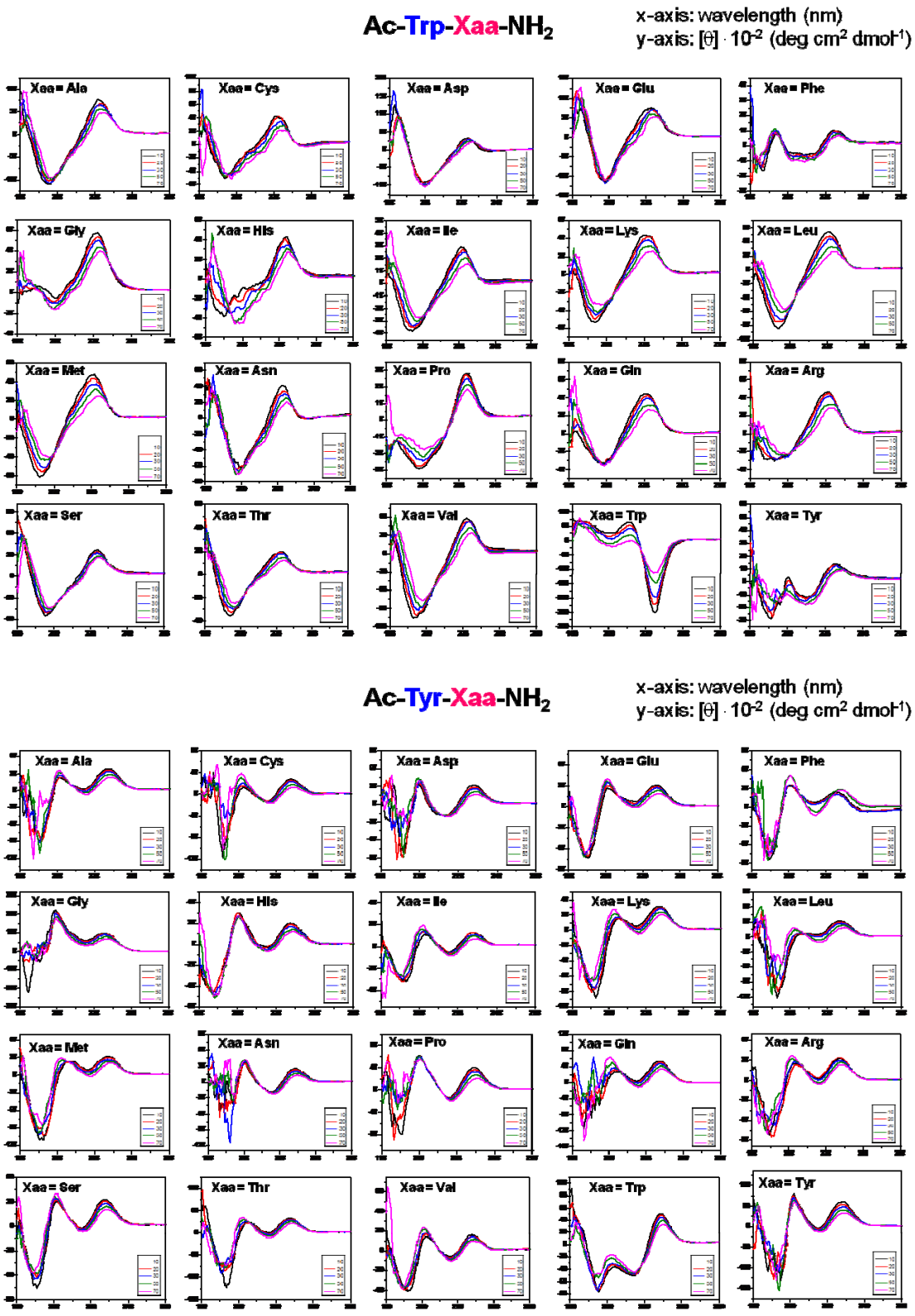

Figure S1: The temperature-dependent CD spectra of dipeptides.

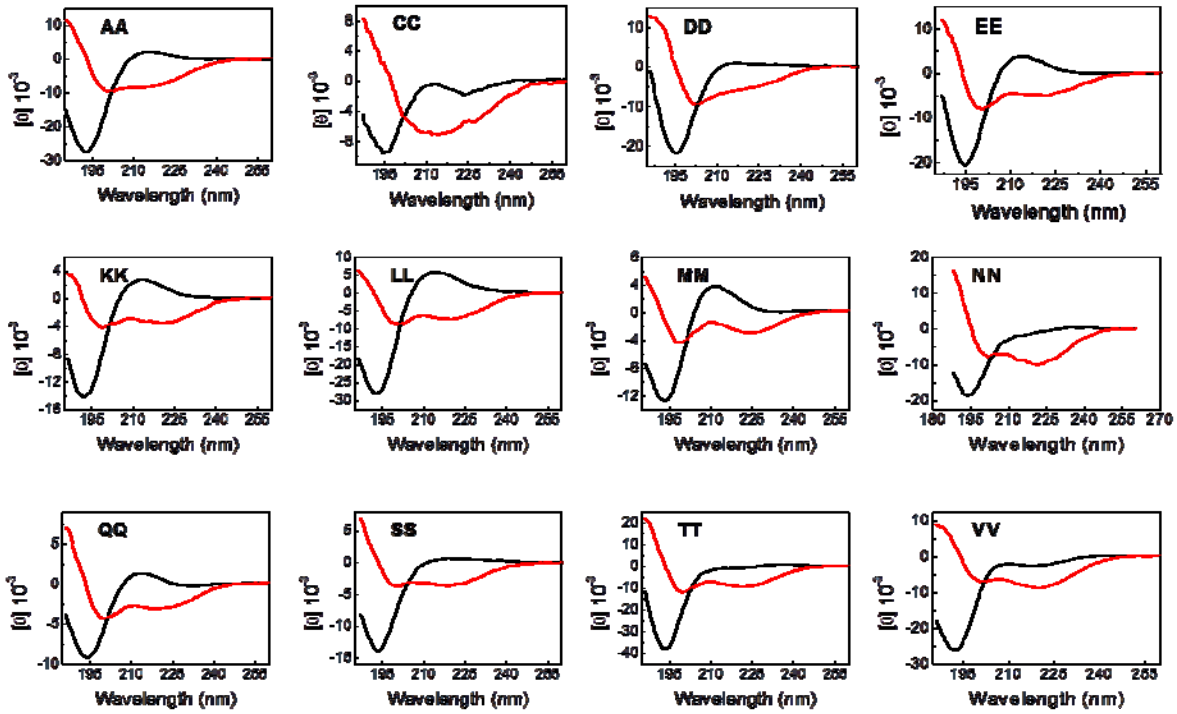

Figure S2: The eigenspectra of P_{II} (black) and β-strand (red) conformers of a few representative dipeptides.

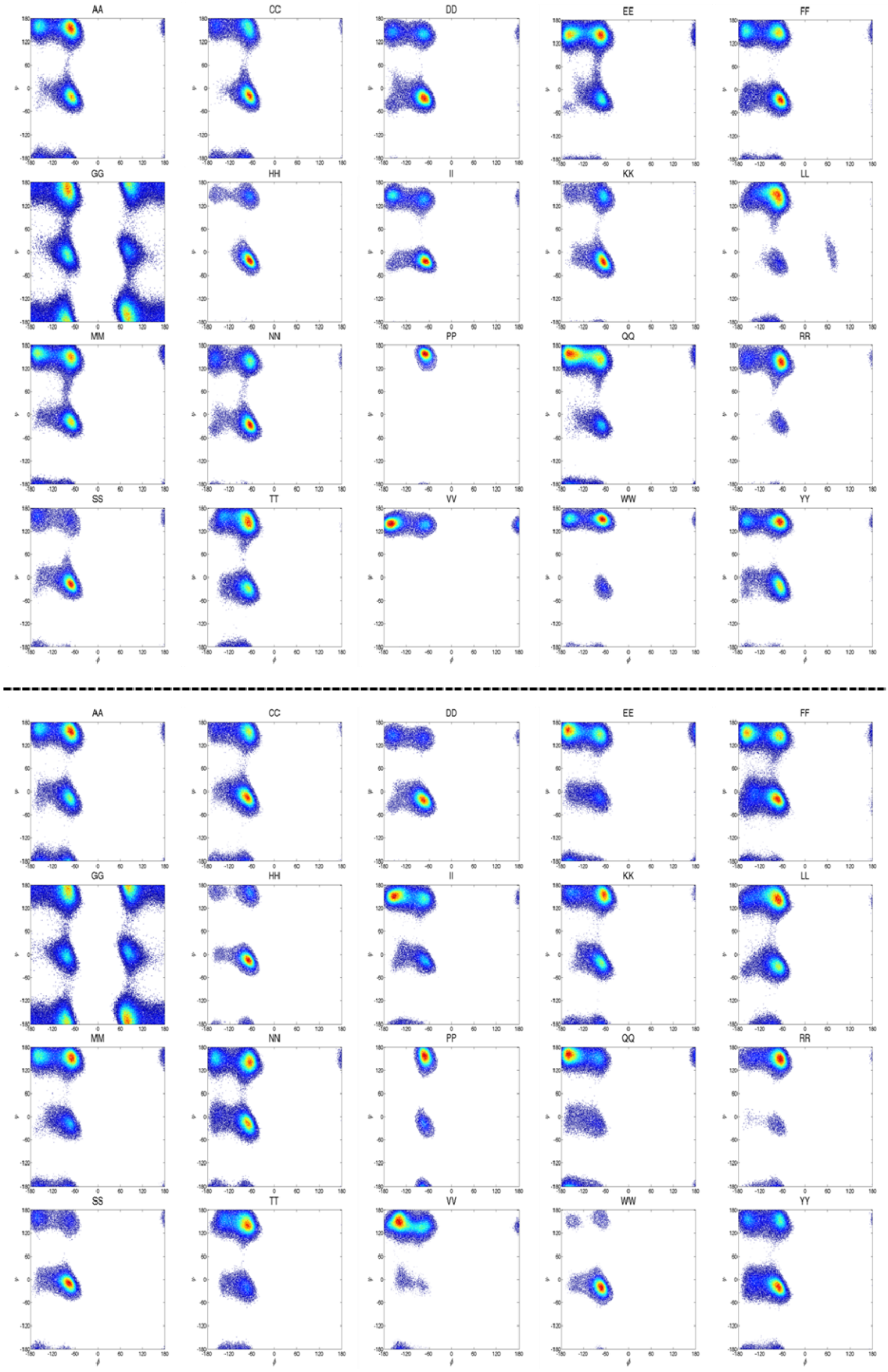

Figure S3: The conformational distribution in the N- (upper) and C-terminal(lower) ϕ,ψ-space.

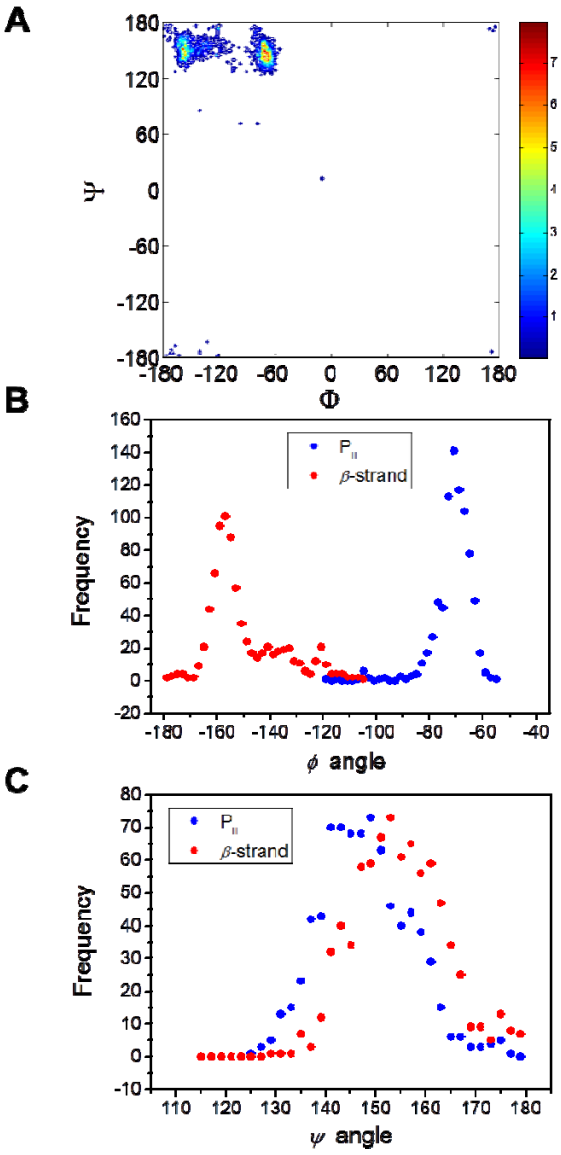

Figure S4: The ϕ,ψ-histogram (**A**) of the P_{II} and β-strand conformers, where the frequency was calculated for every 2°. To determine the percent populations of P_{II}, β-strand, and α-helix from the conformational distribution shown in Fig.S3, we first determined the potential energy barrier between a pair of conformers using the calculated potential of mean force. Now, the ϕ-angle at the transition state between the P_{II} and β-strand conformations is denoted as ϕ^*. Then, the P_{II} domains are assumed to be ($\phi^* < \phi < -20°$, $70° < \psi \leq 180°$) and ($\phi^* < \phi < -20°$, $-180° \leq \psi < -135°$). The β-strand domains are ($-180° \leq \phi < \phi^*$, $80° < \psi \leq 180°$), ($-180° \leq \phi < \phi^*$, $-180° \leq \psi < -150°$), ($160° < \phi \leq 180°$, $80° < \psi \leq 180°$), and ($160° < \phi \leq 180°$, $-180° \leq \psi < -150°$). The right-handed α-helix domain is ($-130° \leq \phi < -30°$, $-70° < \psi < 60°$). In order to determine the ϕ, ψ-angles of each peak in the Ramachandran plots, we considered two dimensional grid with 1^o space. Here, the histograms with respect to ϕ (**B**) and ψ (**C**) are also separately plotted. These are obtained from the P_{II} and β-strand peaks in the conformational distributions of all the dipeptides.