Supporting Information I

Transfer of Noncovalent Chiral Information along an Optically Inactive Helical Peptide Chain: Allosteric Control of Asymmetry of the C-Terminal Site by External Molecule that Binds to the N-Terminal Site

Naoki Ousaka[§] and Yoshihito Inai[†,*]

[§]*Department of Environmental Technology and Urban Planning,* [†]*Department of Frontier Materials, Shikumi College, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

*Correspondence to Y. Inai (inai.yoshihito@nitech.ac.jp)

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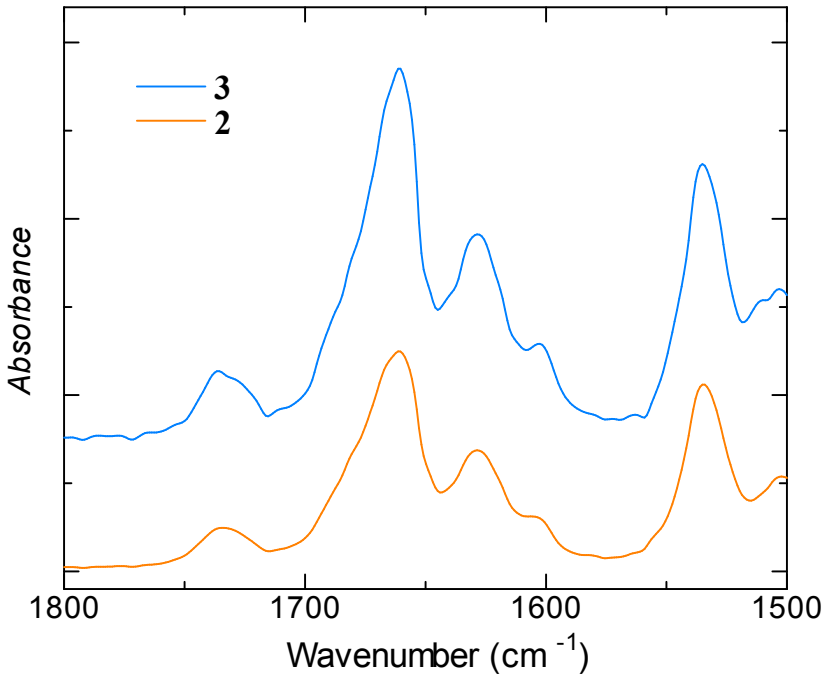

Figure S1. FT-IR absorption spectra of peptides **2** and **3** in chloroform at ambient temperature: [**2**] = 1 mM; [**3**] = 1.8 mM.

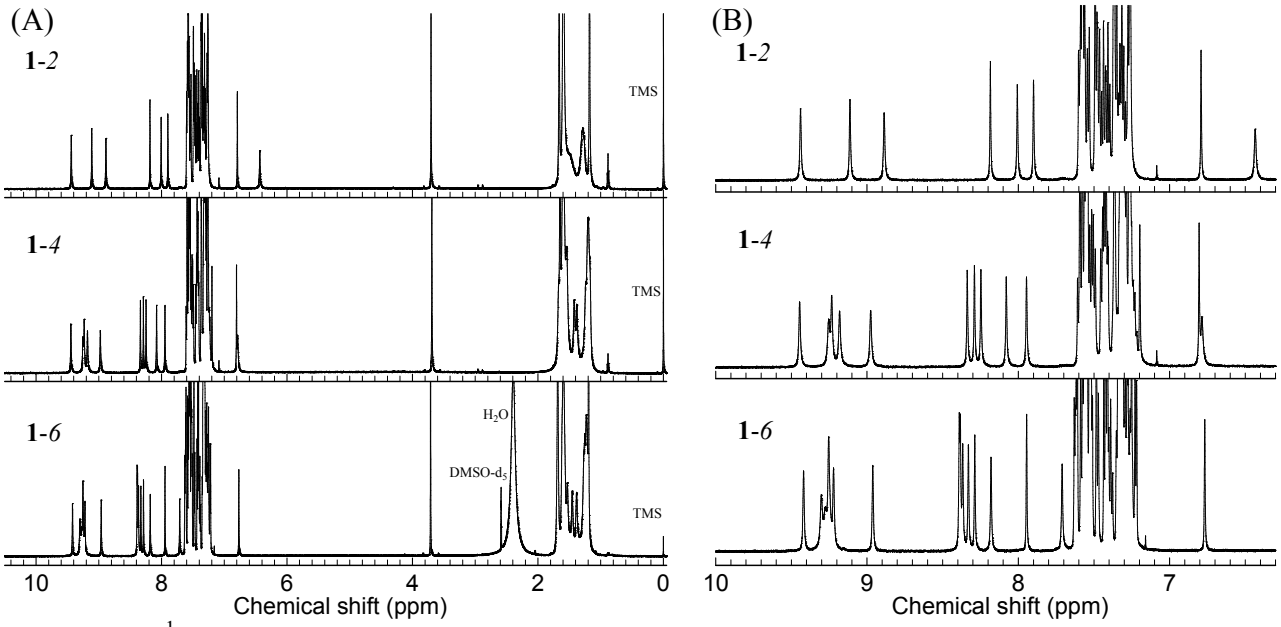

Figure S2. ^{1}H-NMR spectra of peptides **1**-*m* in (A) a wide range and (B) an expanded scale: at 293 K; [peptide] = 3 mM; $CDCl_3$ for *m* = 2 and 4; $CDCl_3/(CD_3)_2SO$ (100/3.7, v/v%) for *m* = 6.

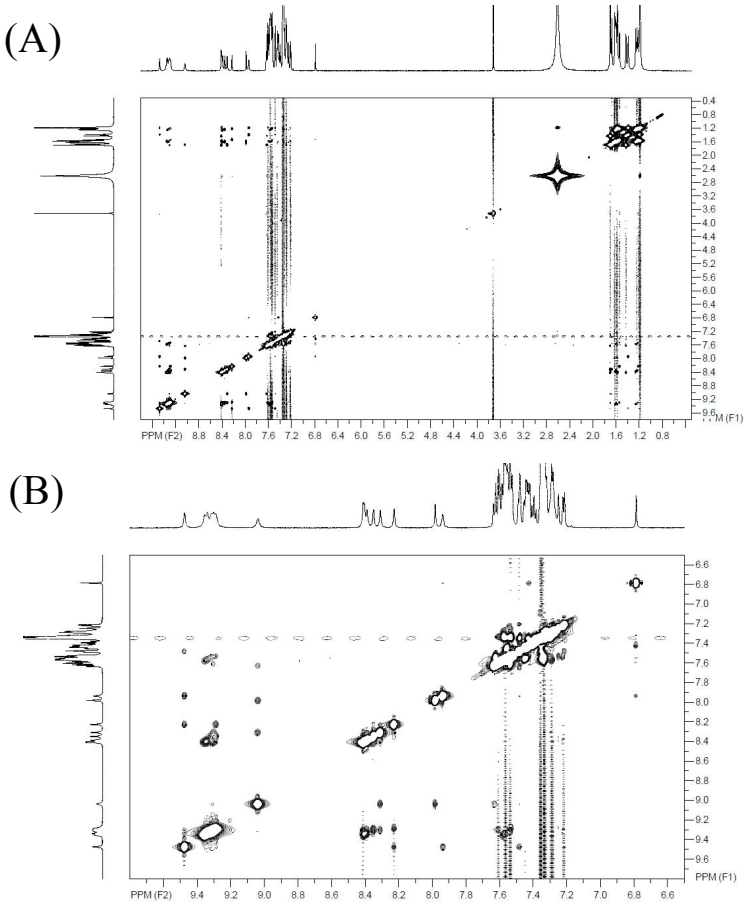

Figure S3. 2D NOESY spectra of peptide **1**-*6* in $CDCl_3/(CD_3)_2SO$ (100/3.7, v/v%) at 273 K: (A) wide region; (B) NH and aromatic region. [**1**-*6*] = 3 mM (prepared at room temperature); mixing time = 0.2 s.

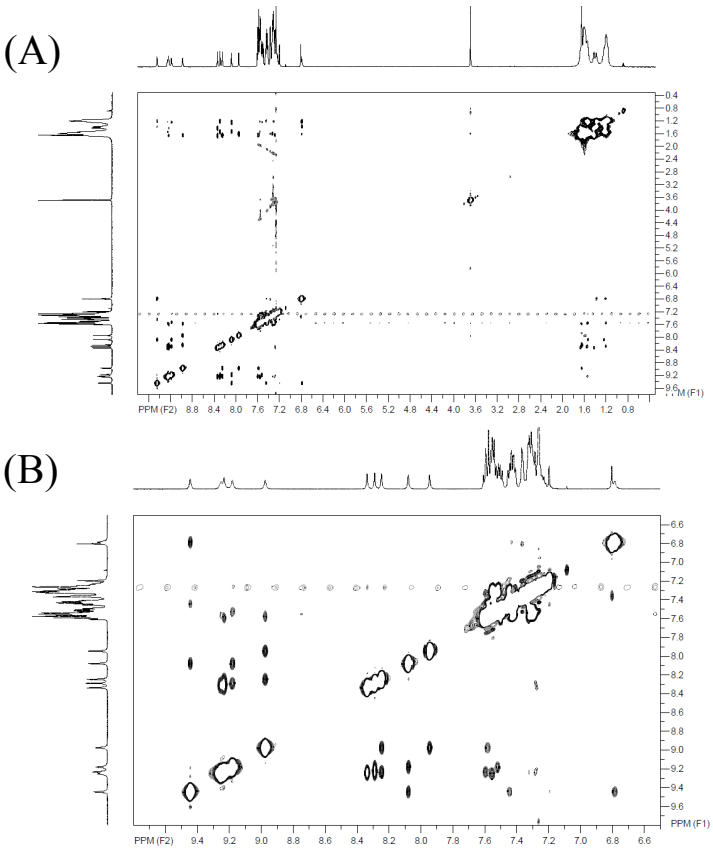

Figure S4. 2D NOESY spectra of peptide **1**-*4* in $CDCl_3$ at 293 K: (A) wide region; (B) NH and aromatic region. [**1**-*4*] = 3 mM; mixing time = 0.4 s.

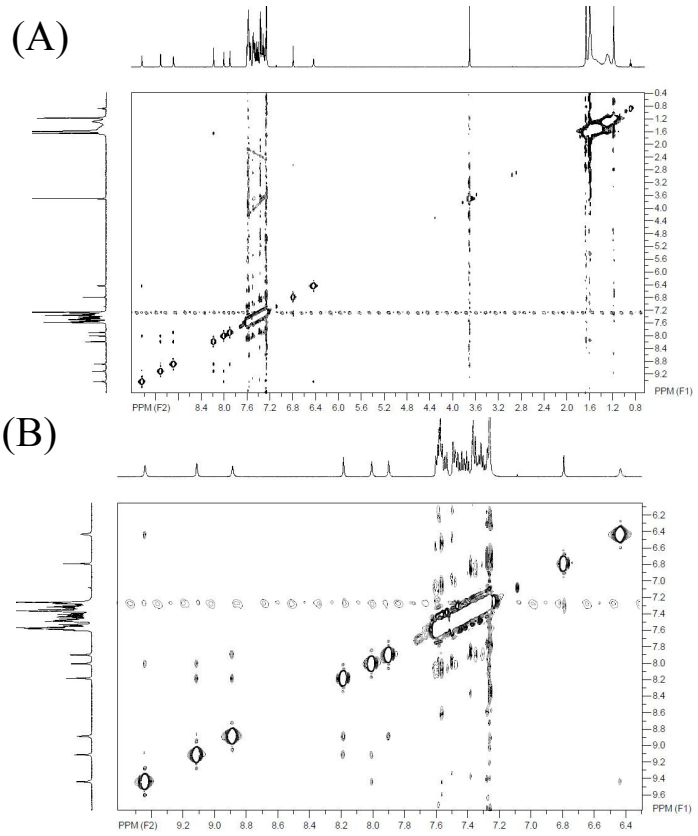

Figure S5. 2D NOESY spectra of peptide **1**-*2* in $CDCl_3$ at 293 K: (A) wide region; (B) NH and aromatic region. [**1**-*2*] = 3 mM; mixing time = 0.4 s.

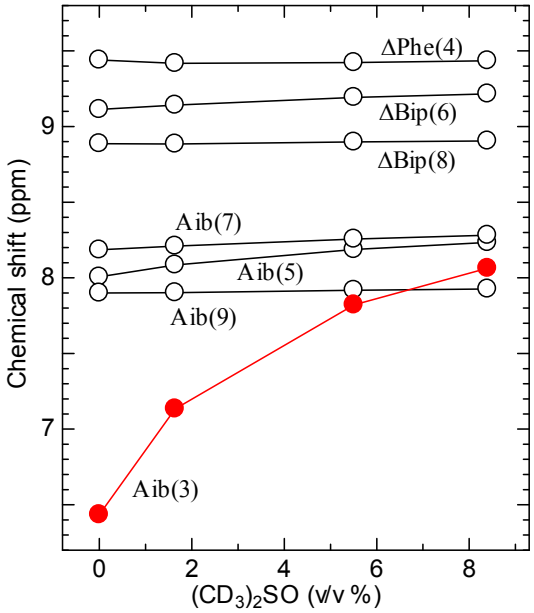

Figure S6. Solvent-composition dependence of NH chemical shifts of **1**-*2* in $CDCl_3/(CD_3)_2SO$ at 293 K: [**1**-*2*] = 3 mM [prior to the addition of $(CD_3)_2SO$].

Table S1. Average values of selected torsion angles and hydrogen-bonding parameters of **1**-*m* in 3_{10}-helix

peptide[a]	helix type	Bip[b]	torsion angles							hydrogen-bonding parameters				
			residues for average	ϕ	ψ	ω	χ^1	χ^2	χ^6	hydrogen-bonding type/ range	O···H (Å)	O···N (Å)	C=O···H (°)	O····H–N (°)
1-*6*	3_{10}-helix	P	2–16	-41	-40	178	-2.5	-45	40	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [14 ← 17]	2.2	3.1	141	161
	3_{10}-helix	M	2–16	-41	-40	178	-2.6	-45	-40	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [14 ← 17]	2.2	3.1	141	161
1-*4*	3_{10}-helix	P	2–12	-41	-40	178	-2.6	-45	40	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [10 ← 13]	2.2	3.1	141	161
	3_{10}-helix	M	2–12	-41	-40	178	-2.6	-45	-40	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [10 ← 13]	2.2	3.0	142	161
1-*2*	3_{10}-helix	P	2–12	-40	-40	177	-2.6	-46	40	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [6 ← 9]	2.2	3.1	142	160
	3_{10}-helix	M	2–12	-40	-40	177	-2.5	-45	-39	$(i)_{CO}\leftarrow(i+3)_{NH}$: from [1 ← 4] to [6 ← 9]	2.2	3.1	143	160

[a]These conformations correspond to Figure 3 and Table 2 (3_{10}-helices). [b]biphenyl orientation (χ^6).

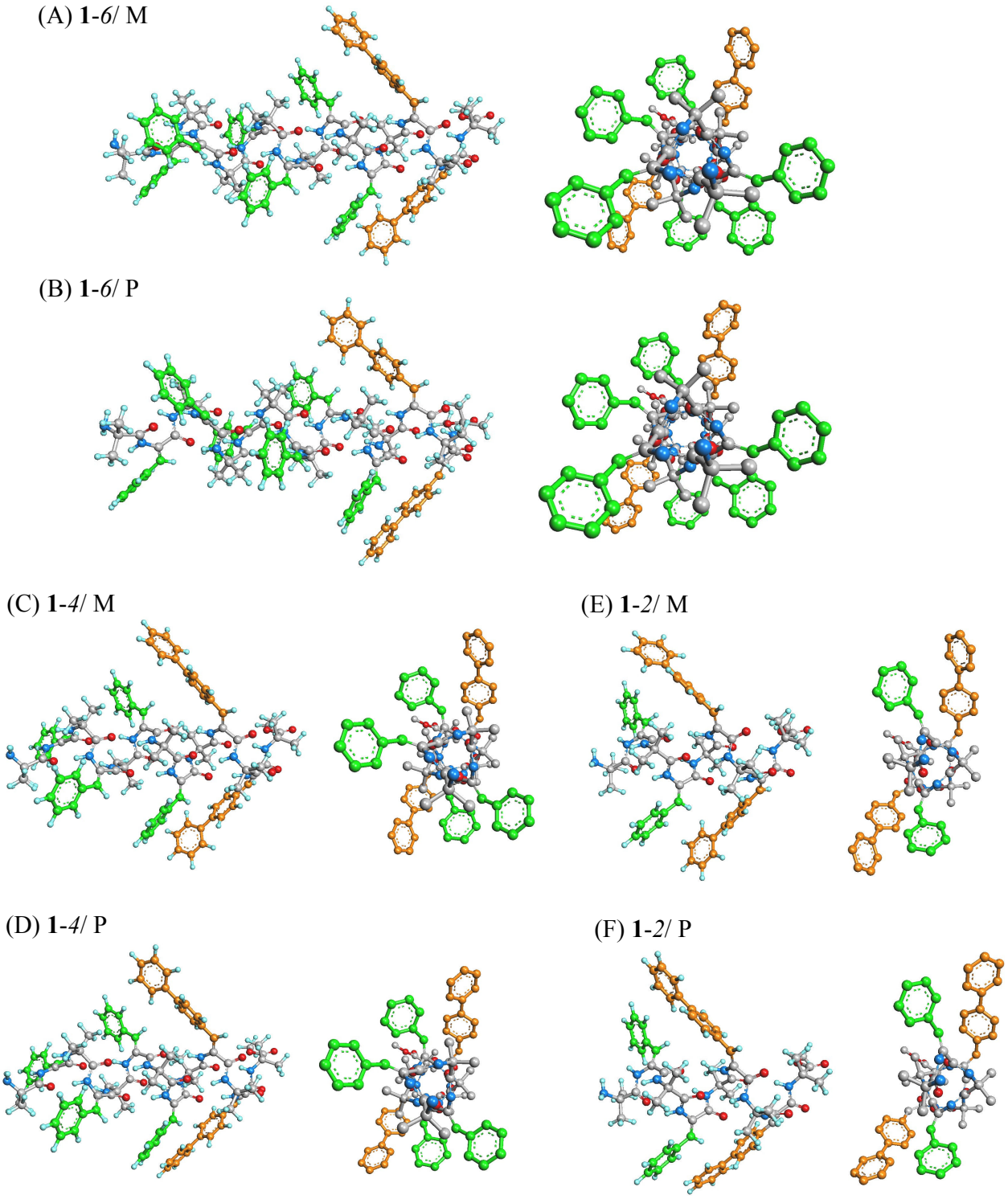

Figure S7. Right-handed helical structures of **1**-*m* energy-minimized from an α-helix: (A, B) **1**-*6*, (C, D) **1**-*4*, and (E, F) **1**-*2*. M and P stand for the two orientations (χ^6) of the biphenyl groups.

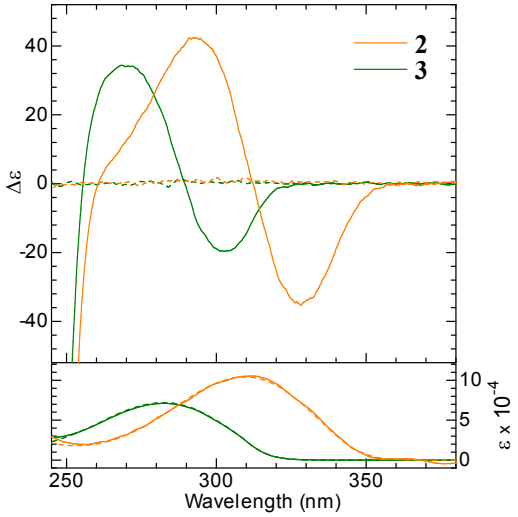

Figure S8. CD spectra of peptides **2** or **3** with (solid line) and without (broken line) Boc-L-proline in chloroform: [**2**] = 0.1 mM; [**3**] = 0.15 mM. CD and absorption spectra of **3** were also reported in ref 10a.

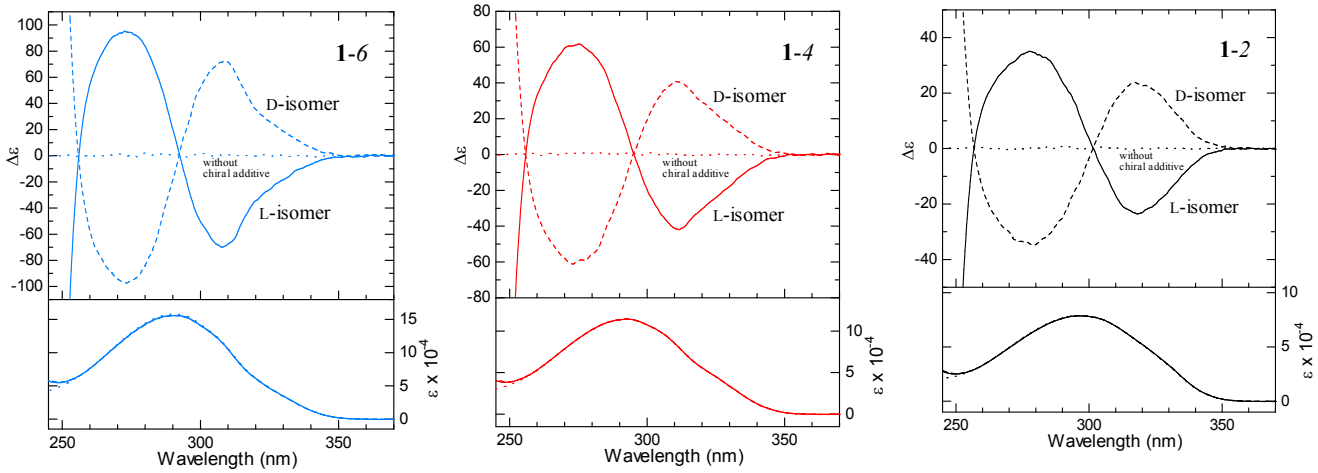

Figure S9. Induced CD spectra of peptides **1**-*m* with Boc-D-proline or Boc-L-proline. The spectra for Boc-L-proline and for no chiral additive correspond to Figure 4.

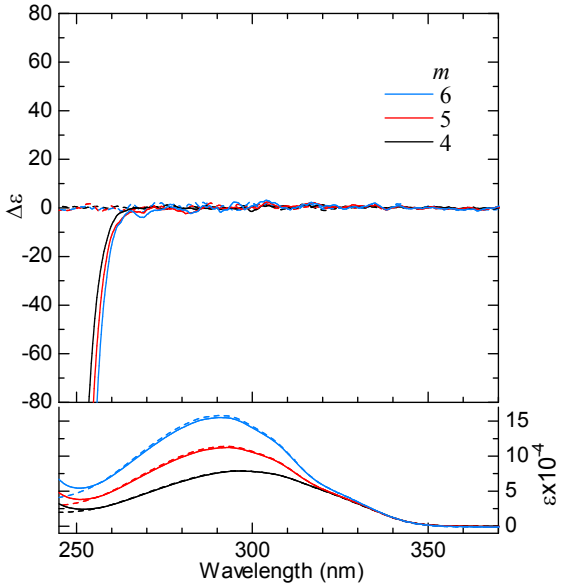

Figure S10. CD spectra of Boc-protected **1**-*m* [Boc-(Aib-Δ^ZPhe)$_m$-(Aib-Δ^ZBip)$_2$-Aib-OMe] (broken line) and with Boc-L-proline (solid line) in chloroform: [**1**-*2*] = 0.13 mM; [**1**-*4*] = 8.9x10^{-2} mM; [**1**-*6*] = 6.2x10^{-2} mM; [Boc-L-proline] = 1.5x10^2 mM.

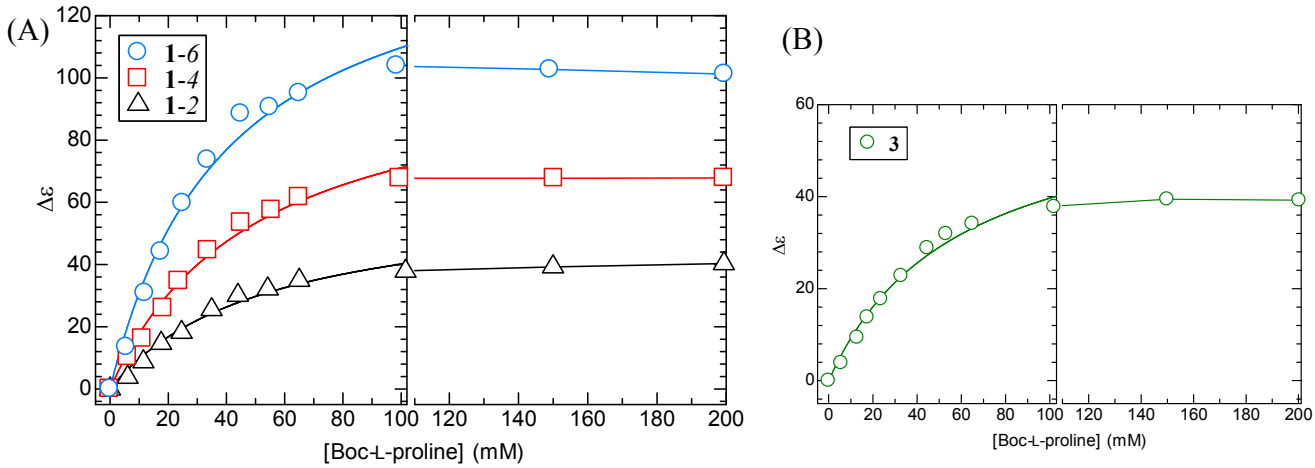

Figure S11. (A) Relationship between the induced CD intensity (Δε) and Boc-L-proline concentration in chloroform at ambient temperature: [**1**-*6*] = 6.3x10^{-2} mM; [**1**-*4*] = 9.0x10^{-2} mM; [**1**-*2*] = 1.3x10^{-1} mM. The CD intensity indicated Δε value at 272.8 nm (**1**-*6*), 274.8 nm (**1**-*4*), and 278.4 nm (**1**-*2*). In the left panel, the curve was obtained from nonlinear fitting for estimation of the binding constant (see ref 39). (B) A similar experiment for **3**–Boc-L-proline monitoring Δε at 270 nm: [**3**] = 0.15 mM. (The concentration dependence of chiral additive was similar to that already reported in ref 10a.) In (A) and (B), Δε value at [Boc-L-proline] = 0 mM was treated as zero.

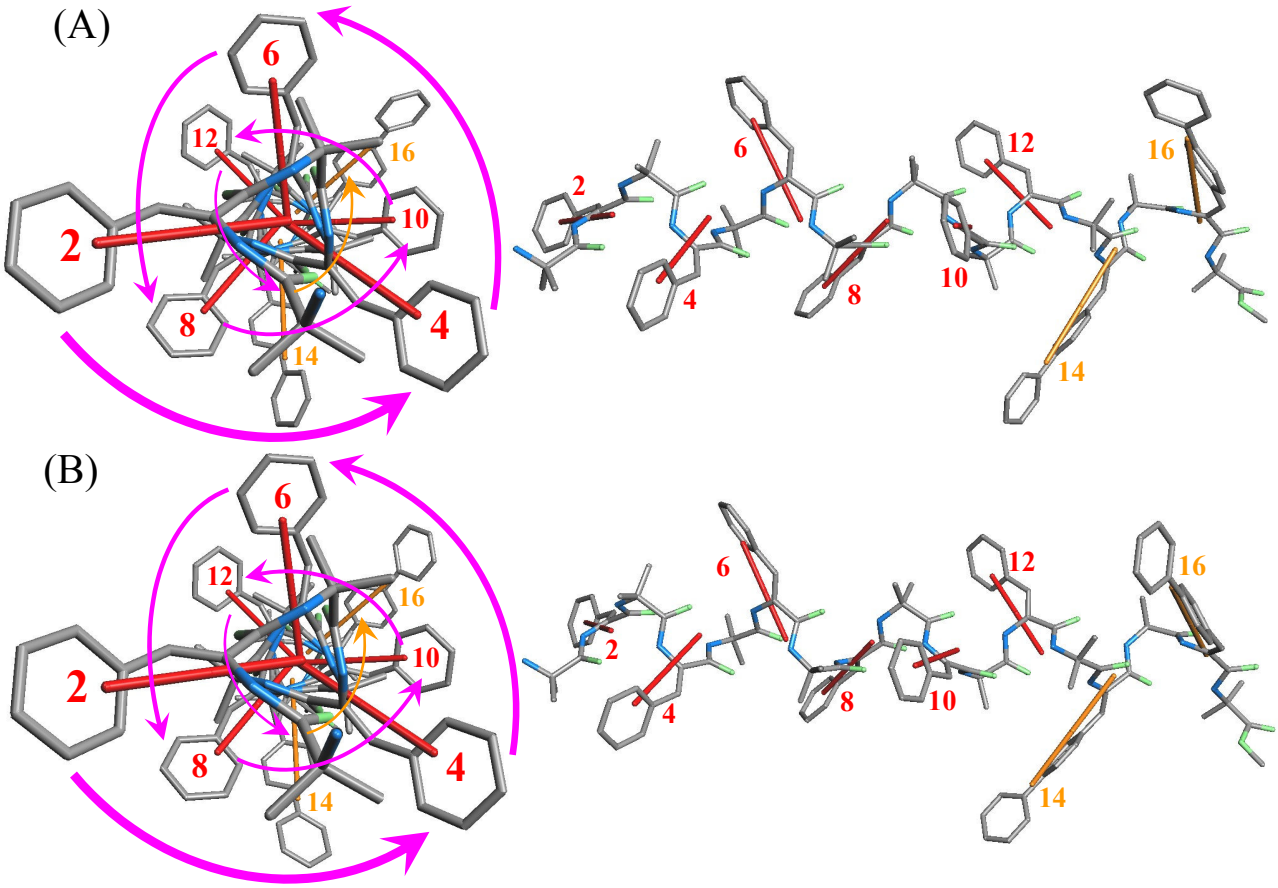

Figure S12. Spatial arrangement of each ΔAA residue TDM (in the length form) along the right-handed 3_{10}-helix of **1**-*6*: (A) and (B) correspond to Figures 3A and 3B with the two types of Δ^{Z}Bip side-chain orientations. The right-handed helix produces a left-handed twist of the neighboring moments with respect to the helical axis.