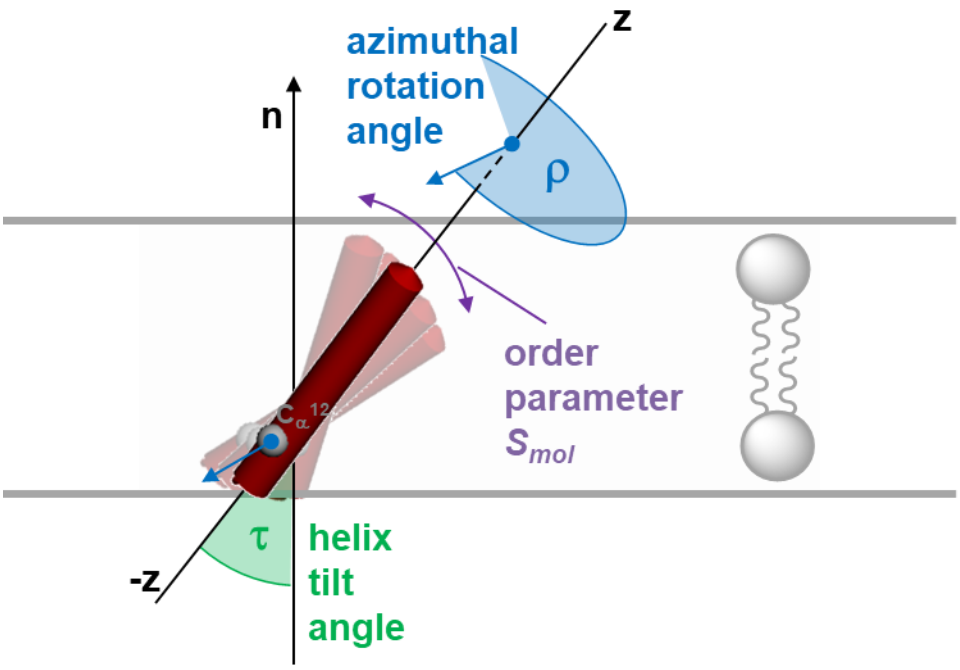

Figure S1. *Definition of the angles* ***τ*** *and ρ, which describe the orientation of a peptide molecule with respect to the lipid bilayer normal* ***n****. The long axis,* ***z****, is defined by the longest director of a secondary structure motif (helix, strand, N-to-C direction).* C_a *of an amino acid at position 12 defines the rotational angle* ***ρ****.*

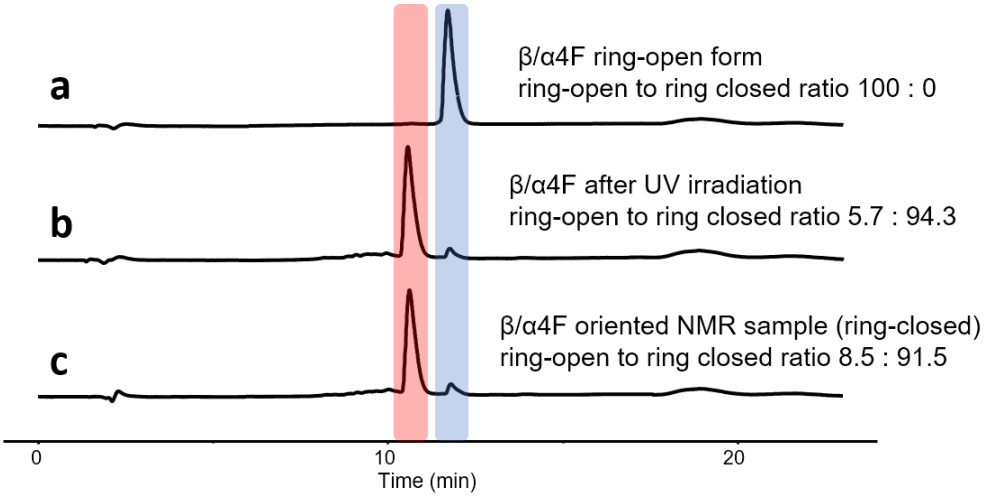

Figure S2. *Example analytical RP-HPLC of the conjugate β/α4F in the flexible (ring-open) form before irradiation with UV light (a) and in the rigid (ring-closed) form after photoswitching (b). The chromatogram of the conjugate β/α4F in the ring-closed form extracted from the NMR sample after carrying out the NMR measurements (c). For each chromatogram the observed ratio between ring-open and ring-closed forms is given.*

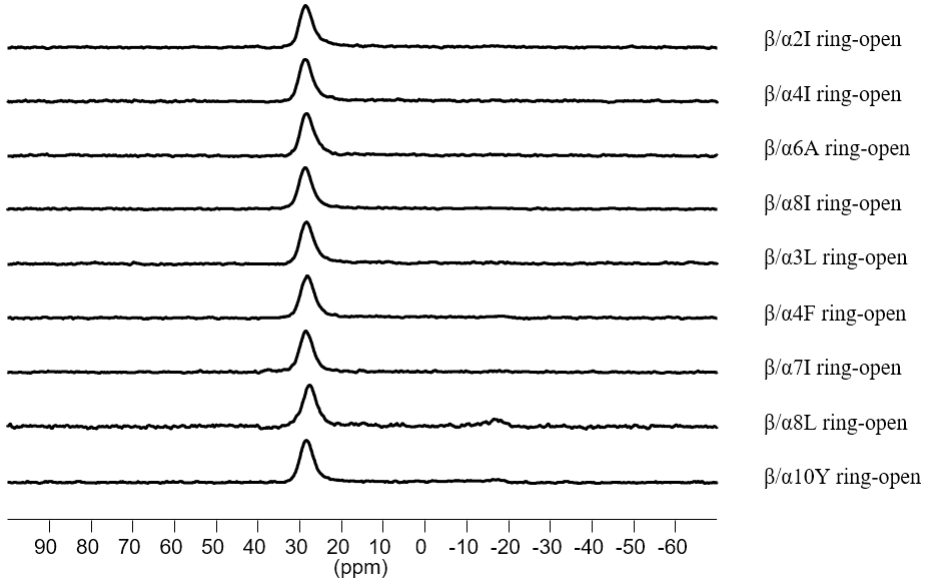

***Figure S3**. Solid-state ^{31}P-NMR spectra of the β/α-model labeled with Bpg. Conjugates were reconstituted in oriented DMPC bilayers (P/L = 1:100) and measured at 40 °C in the flexible forms.*

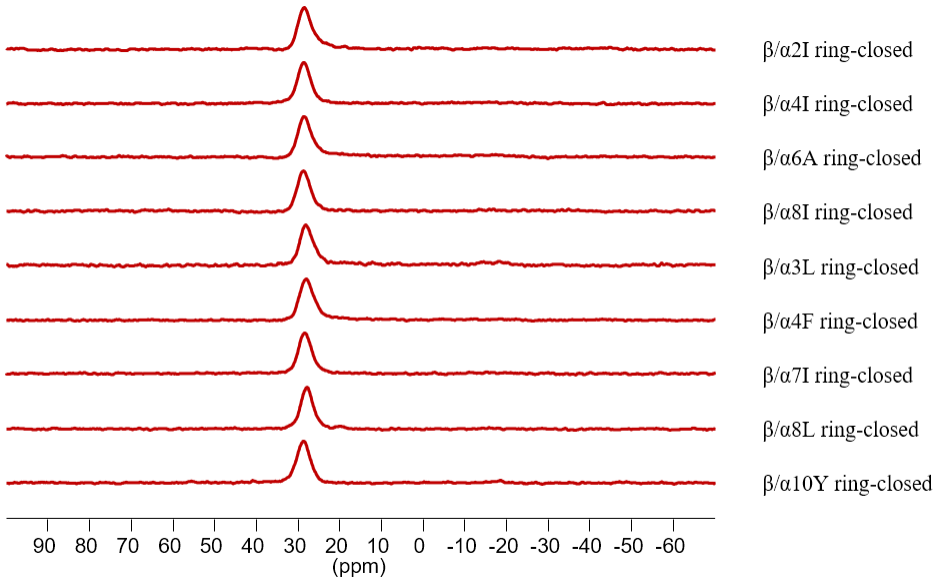

Figure S4. *Solid-state ^{31}P-NMR spectra of the β/α-model labeled with Bpg. Conjugates were reconstituted in oriented DMPC bilayers (P/L = 1:100) and measured at 40 °C in the rigid forms.*

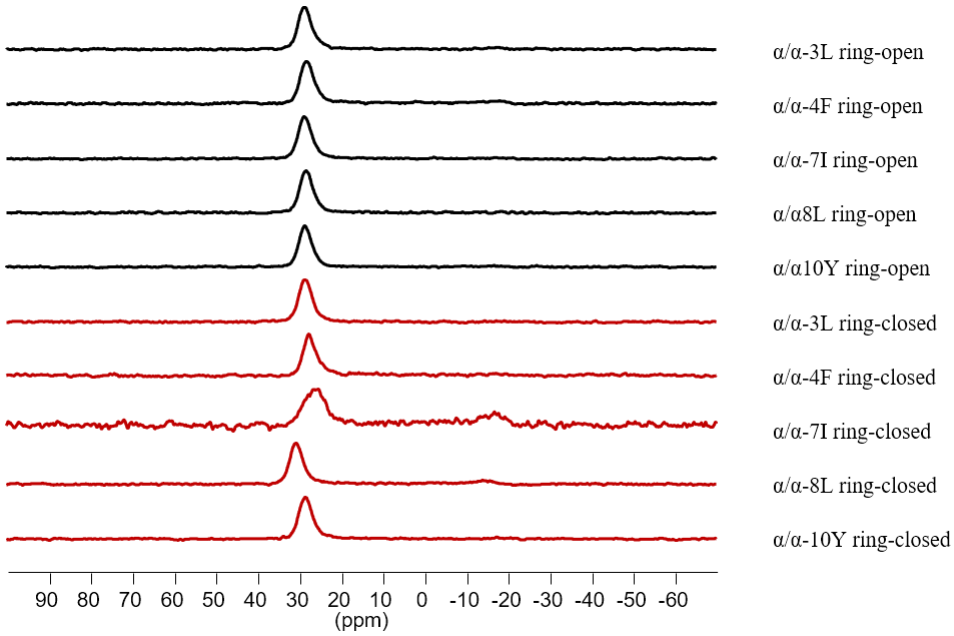

Figure S5. *Solid-state ^{31}P-NMR spectra of the α/α-model labeled with Bpg. Conjugates were reconstituted in oriented DMPC bilayers (P/L = 1:100) and measured at 40 °C in the rigid (red lines) and flexible (black lines) forms.*