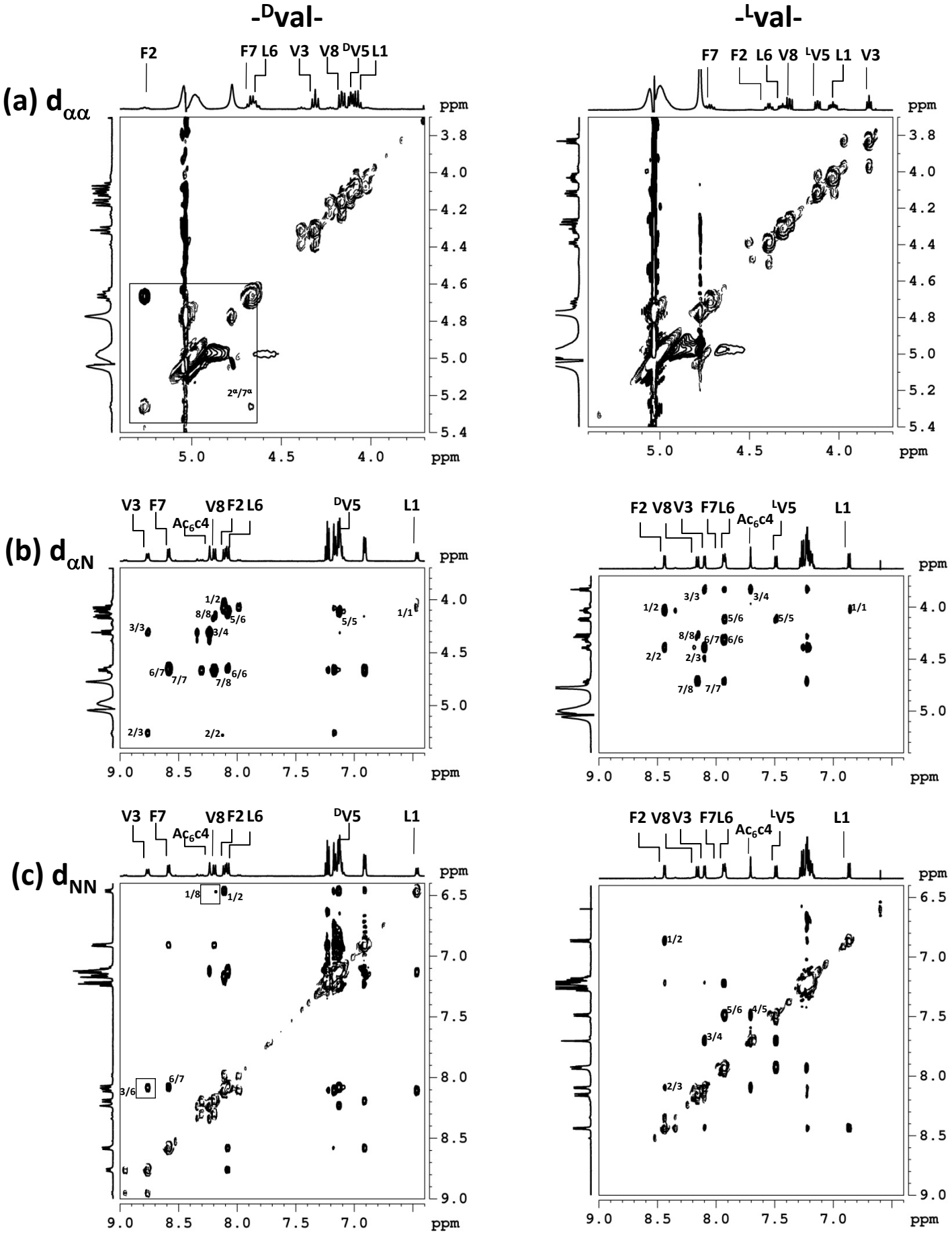


Figure S1: Partial ROESY spectra of peptides **1** (right) and 2 (left). (a) C^{α} proton region, (b) NH-C^{α}H region (c) NH-NH region. Long range NOEs are boxed.

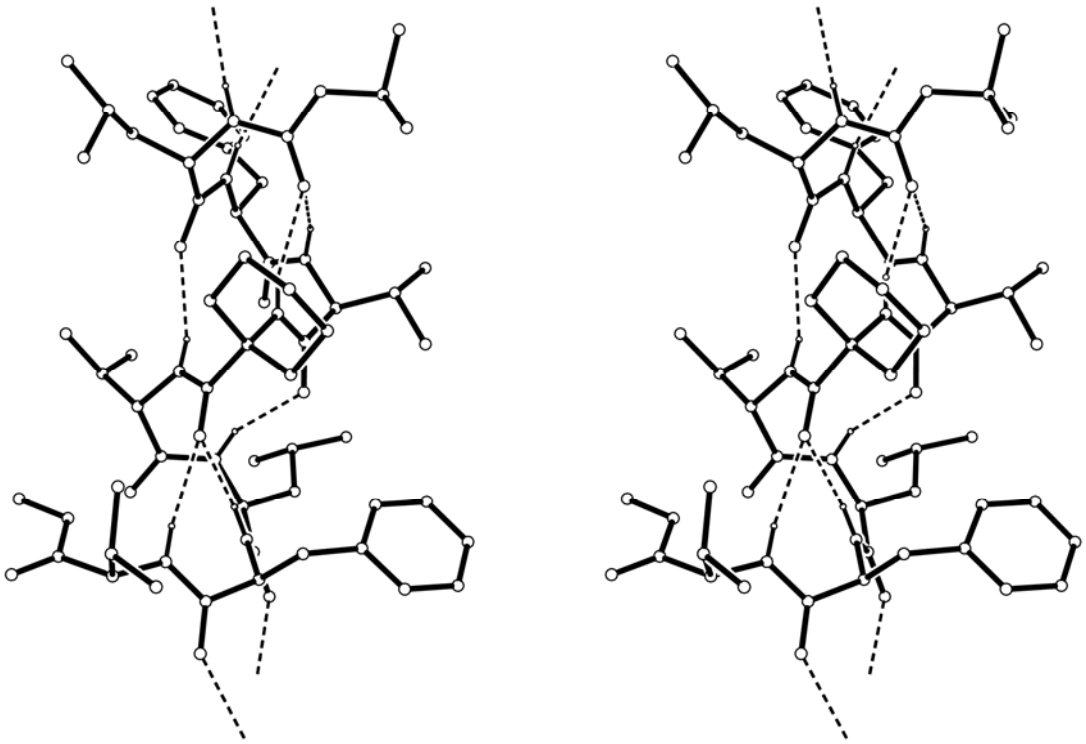
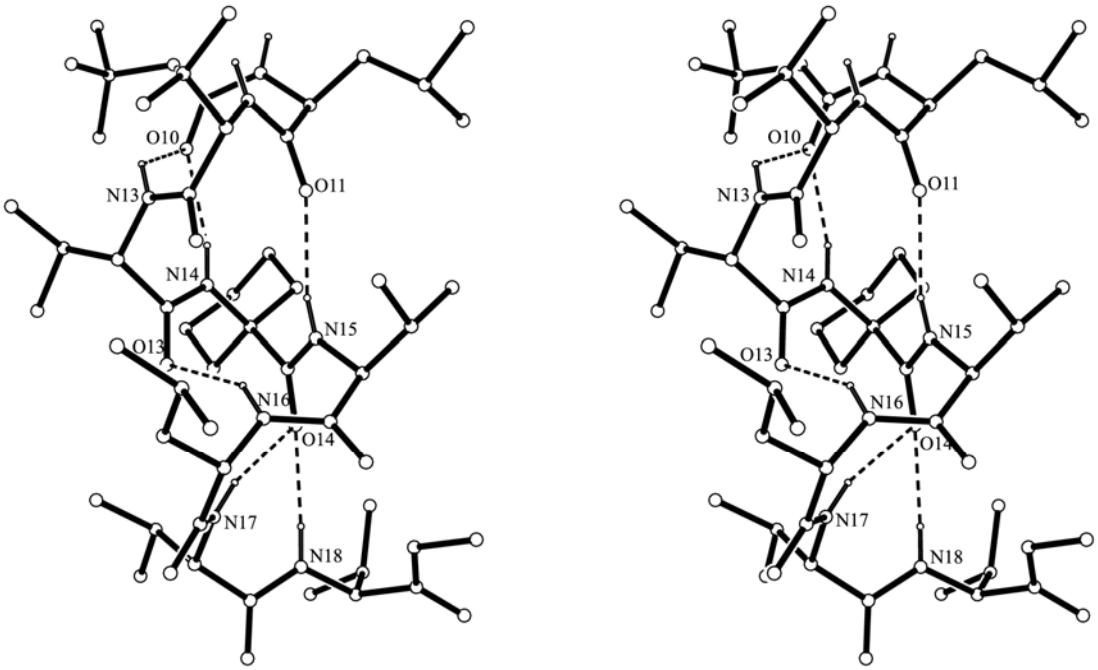
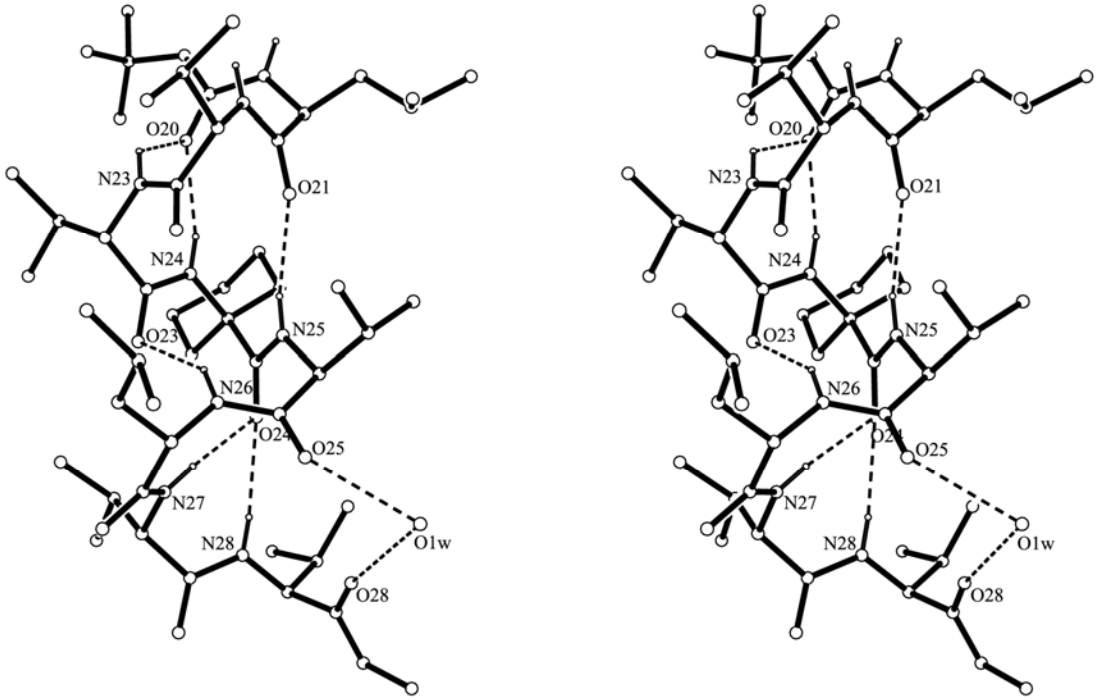


Figure S2: Stereoview of molecular conformation of Boc-Leu-Phe-Val-Ac_6c-Val-Leu-Phe-Val-OMe (**2**) in crystals. The intramolecular hydrogen bonds are shown in dashed lines



Molecule-A



Molecule-B

Figure S3: Stereoview of molecular conformation of the two Molecules A and B in the asymmetric unit of Boc-Leu-Val-Val-Ac$_6$c-Val-Leu-Val-Val-OMe (**4**) in crystals. The intramolecular hydrogen bonds are shown in dashed lines.

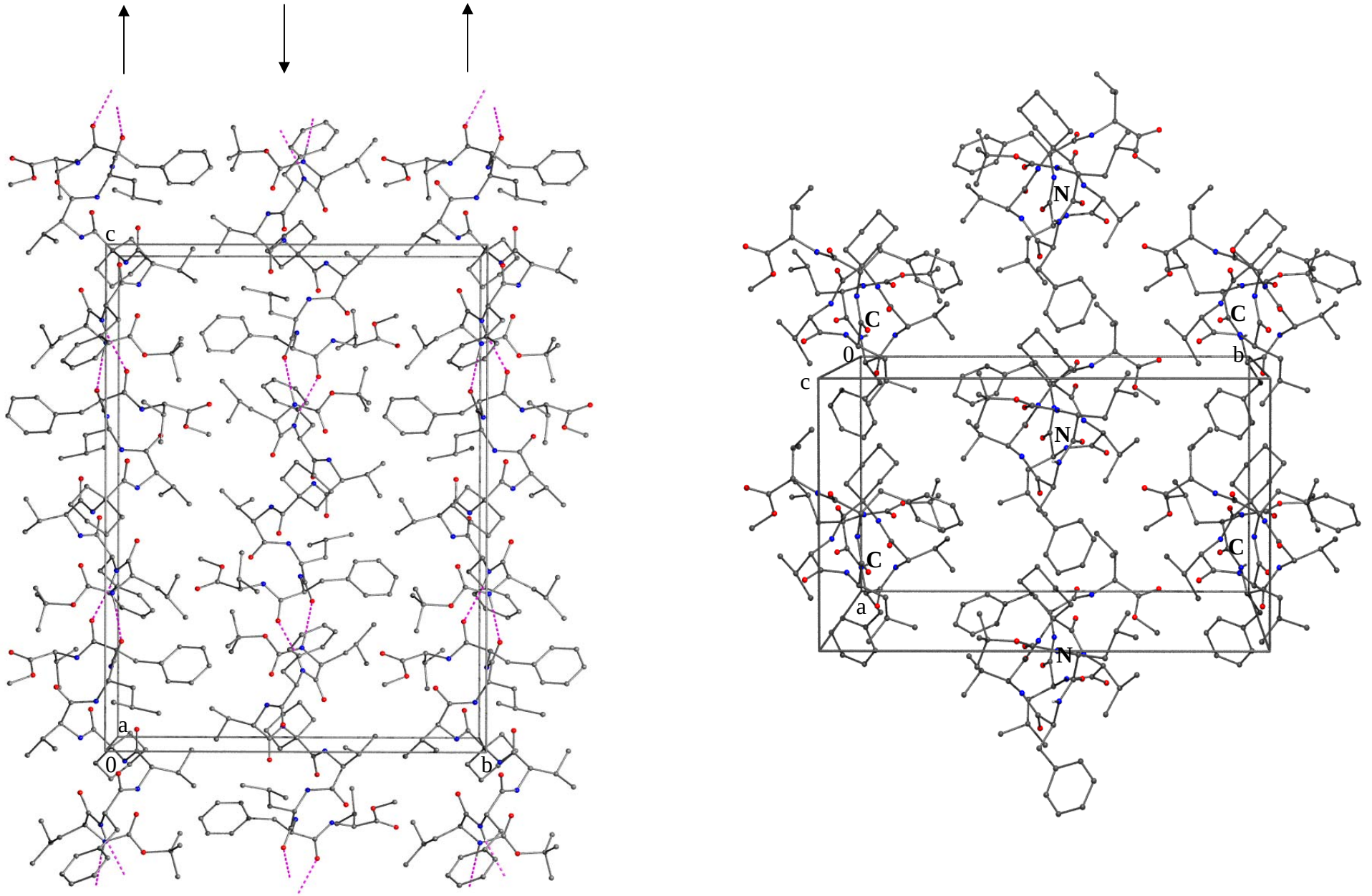


Figure S4. (Left) Molecular packing of Peptide **2** in crystals. The arrows indicate the direction of helix axis and mode of association. The intermolecualr hydrogen bonds are shown as dotted lines. (Right) Packing of helices, as viewed down the helix axis, indicating pseudohexagonal grid arrangement in crystals

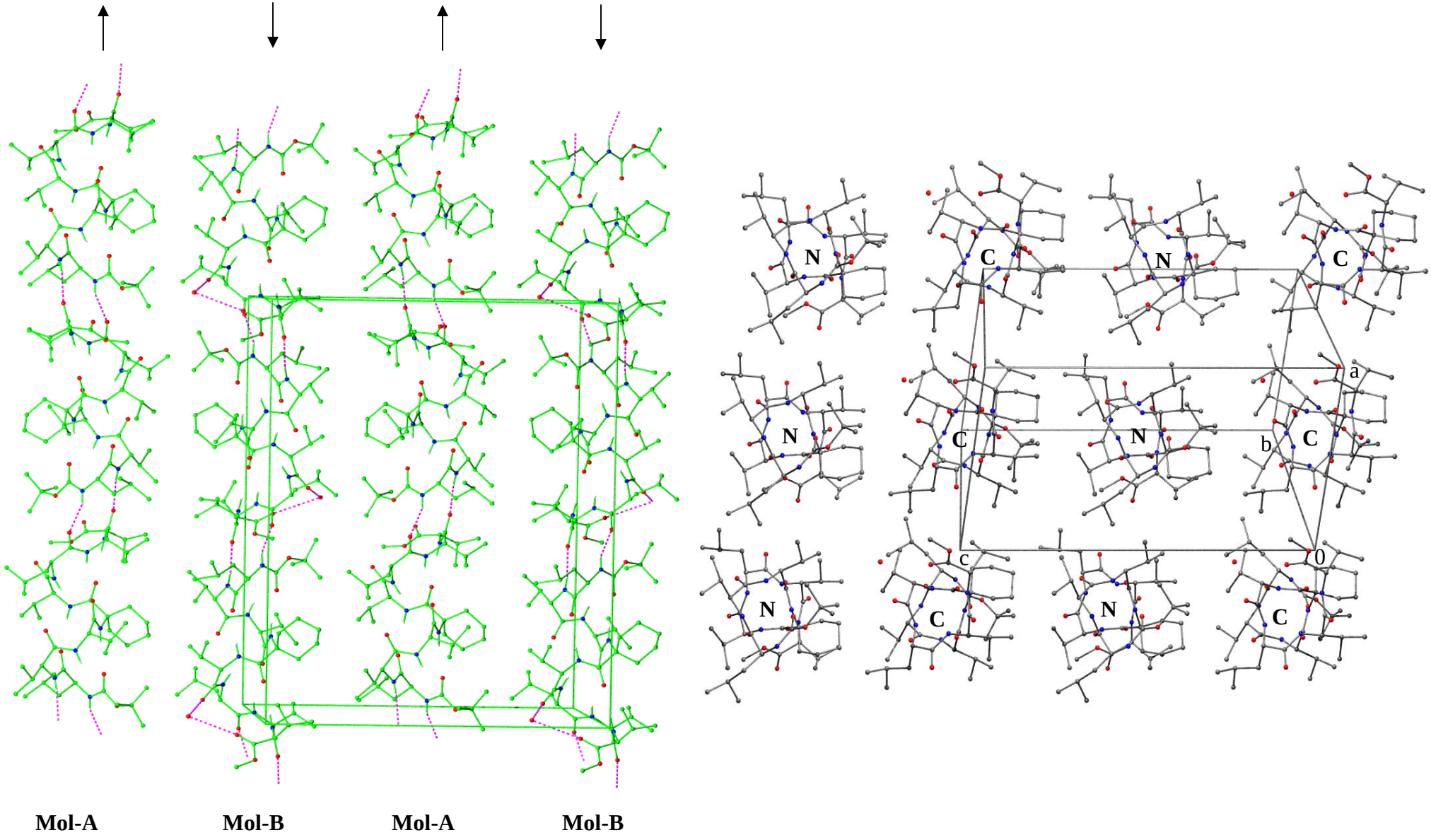


Figure S5. (Left) Molecular packing of Peptide **4** in crystals. The arrows indicate the direction of helix axis and mode of association. The intermolecualr hydrogen bonds are shown as dotted lines. (Right) Packing of helices, as viewed down the helix axis, indicating a square grid arrangement in crystals

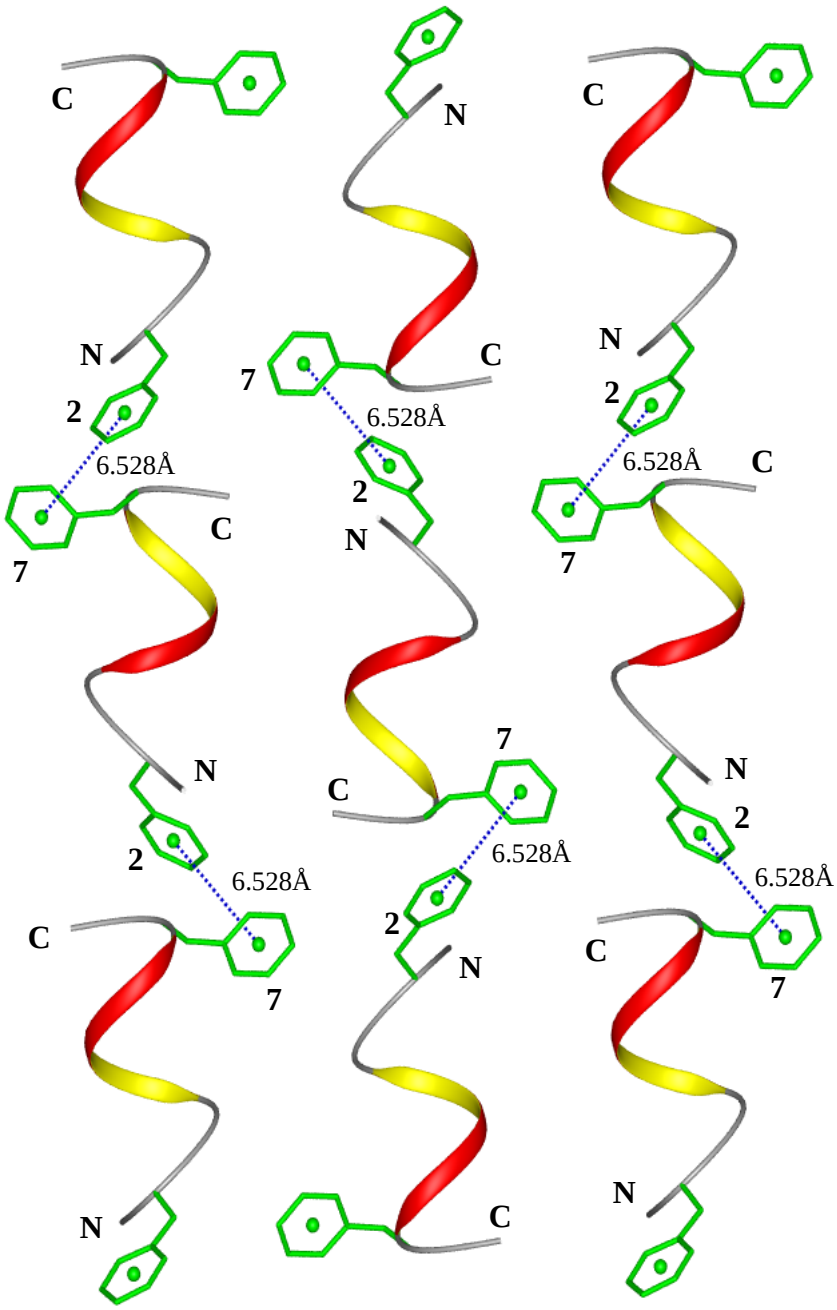


Figure S6. Schematic view of Phe-Phe interactions stabilizing the column of helices in crystals of peptide **2**. The molecular backbone is shown as a ribbon representation, and the centroid-to-centroid distance (Å) between proximal aromatic rings are marked. The interplanar angle is 88.27°