Supporting Information for:

Crystallographic Characterization of 12-Helical Secondary Structure in β-Peptides Containing Side Chain Groups

Soo Hyuk Choi, Ilia A. Guzei, Lara C. Spencer and Samuel H. Gellman*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Synthesis

Boc-ACPC-OH was prepared by the method in reference 5c. β-Peptides **1-5** were synthesized by a conventional fragment coupling strategy analogous to the method described in references 12c and 12d. Boc-β^3-hPhe-OH, 4-dimethylaminopyridine (DMAP) and 1-Ethyl-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) were purchased from Sigma-Aldrich or Chem-Impex International Inc.

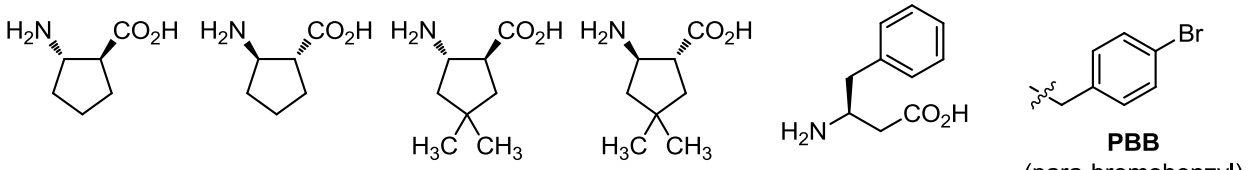
General procedure for peptide coupling. To a 0.1 M solution of an amine (1 equiv) and an acid (1 equiv) in *N,N*-dimethylformamide (DMF), EDCI (1.5 equiv) and DMAP (1.1 equiv) are added, and the reaction mixture is stirred at rt for 3 d.

General work-up procedure. After the coupling reaction is complete, the reaction mixture is diluted with excess ethyl acetate (EtOAc) and then washed with 10% aqueous citric acid, aqueous saturated $NaHCO_3$, and brine. The organic layer is then dried over $MgSO_4$, filtered and concentrated to give a crude product, which is purified by silica gel chromatography.

General procedure for deprotection of a Boc group. A *N*-Boc protected oligomer is treated with 4.0 M HCl in dioxane (*ca*. 10 equiv) for 30 min with stirring, and the mixture is then concentrated under a nitrogen gas stream to give the HCl salt form of the amine segment.

General procedure for saponification of a C-terminal ester group. To 0.1 M solution of a methyl or ethyl ester in MeOH/H_2O (v/v = 2/1), LiOH·H_2O (5 equiv) is added at 0 ^oC. The mixture is stirred for 6 h at 0 ^oC. After most of the solvent is evaporated by a nitrogen gas stream, aqueous 1 M HCl is added until pH ~2. The turbid mixture is extracted with EtOAc. The combined organic fraction is washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give the carboxylic acid form, which is used without purification.

General Procedure for benzyl ester formation. To a 0.1 M solution of a peptide carboxylic acid (1 equiv) in acetonitrile, benzyl bromide (2 equiv) and K_2CO_3 (3 equiv) are added. The mixture is stirred for 12 h, and diluted with excess EtOAc. The desired product is obtained by the general work-up procedure described above.



ACPC **ent-ACPC** **dm-ACPC** **ent-dm-ACPC** **β³-hPhe** **PBB** (para-bromobenzyl)

Boc-*dm*-ACPC-OMe (7) was prepared by a method analogous to that described in reference 4j of the main text. ^1H NMR (300 MHz, $CDCl_3$) δ 4.59 (br s, 1H), 4.23 (quintet, J = 8.6 Hz, 1H), 3.69 (s, 3H), 2.67 (q, J = 9.3 Hz, 1H), 2.01 (dd, J = 12.9, 7.6 Hz, 1H), 1.78 (m, 2H), 1.43 (s, 9H), 1.35 (dd, J = 12.9, 9.7 Hz, 1H), 1.08 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.12, 155.44, 55.69, 52.09, 51.17, 47.96, 43.27, 43.13, 36.98, 30.81, 30.21, 28.54; ESI-TOF MS *m/z* calculated for $C_{14}H_{25}NO_4$ 271.1, found 272.2 $[M+H]^+$, 294.2 $[M+Na]^+$, 565.3 $[2M+Na]^+$.

Boc-(*dm*-ACPC)$_2$-OMe (8) was prepared from monomer **7** by general procedures (saponification, deprotection of Boc group and peptide coupling). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (br s, 1H), 4.67 (d, *J* = 7.8 Hz, 1H), 4.46 (quintet, *J* = 8.4 Hz, 1H), 4.12 (quintet, *J* = 8.0 Hz, 1H), 3.59 (s, 3H), 2.75 (q, *J* = 9.2 Hz, 1H), 2.58 (q, *J* = 8.2 Hz, 1H), 1.95-1.78 (m, 3H), 1.77-1.65 (m, 3H), 1.38 (s, 9H), 1.34 (dd, *J* = 12.5, 8.7 Hz, 1H), 1.23 (dd, *J* = 12.6, 8.5 Hz, 1H), 1.02 (s, 3H), 1.01 (s, 3H), 0.99 (s, 3H), 0.92 (s, 3H); ESI-TOF MS *m/z* calculated for $C_{22}H_{38}N_2O_5$ 410.3, found 411.2 $[M+H]^+$, 433.2 $[M+Na]^+$, 843.5 $[2M+Na]^+$.

Boc-(*dm*-ACPC)$_4$-OMe (1) was prepared from dipeptide **8** by a fragment condensation strategy. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.55 (quintet, *J* = 8.3 Hz, 1H), 4.45 (quintet, *J* = 7.8 Hz, 1H), 4.43 (quintet, *J* = 7.8 Hz, 1H), 4.18 (quintet, *J* = 8.3 Hz, 1H), 3.66 (s, 3H), 2.92 (q, *J* = 9.1 Hz, 1H), 2.77-2.52 (m, 3H), 2.08-1.61 (m, 12H), 1.44 (s, 9H), 1.54-1.22 (m, 4H), 1.09 (s, 3H), 1.08 (s, 3H), 1.07 (br s, 6H), 1.06 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H); ESI-TOF MS *m/z* calculated for $C_{38}H_{64}N_4O_7$ 688.5, found 689.5 $[M+H]^+$, 711.5 $[M+Na]^+$.

Boc-ACPC-*dm*-ACPC-OMe (9) was prepared from Boc-ACPC-OH and Boc-*dm*-ACPC-OMe. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (br s, 1H), 4.67 (br s, 1H), 4.52 (quintet, *J* = 8.3 Hz, 1H), 3.96 (quintet, *J* = 6.3 Hz, 1H), 3.66 (s, 3H), 2.81 (q, *J* = 9.0 Hz, 1H), 2.58 (m, 1H), 2.17-1.59 (m, 10H), 1.46 (s, 9H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.34, 173.41, 156.62, 80.28, 56.72, 54.25, 53.40, 52.05, 51.01, 47.55, 46.29, 43.40, 33.72, 30.43, 30.15, 28.61, 27.57, 24.38; ESI-TOF MS *m/z* calculated for $C_{20}H_{34}N_2O_5$ 382.3, found 383.2 $[M+H]^+$, 405.3 $[M+Na]^+$.

Boc-ACPC-*dm*-ACPC-OBn (10) was prepared from methyl ester **9** by general procedures (saponification and benzyl ester formation). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (br s,

1H), 7.40-7.22 (m, 5H), 5.11 (ABq, J_{AB} = 12.5 Hz, $\Delta\upsilon$ = 0.09 ppm, 2H), 4.63 (br s, 1H), 4.56 (quintet, *J* = 8.3 Hz, 1H), 3.83 (quintet, *J* = 6.2 Hz, 1H), 2.89 (q, *J* = 9.0 Hz, 1H), 2.55 (m, 1H), 2.10-1.51 (m, 10H), 1.45 (s, 9H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.79, 173.32, 156.59, 136.51, 128.61, 128.24, 128.13, 80.22, 66.57, 56.63, 54.25, 53.33, 51.00, 47.64, 43.41, 37.64, 33.63, 30.32, 30.03, 28.59, 27.54, 24.3; ESI-TOF MS *m/*z calculated for $C_{26}H_{38}N_2O_5$ 485.3, found 459.3 $[M+H]^+$, 481.2 $[M+Na]^+$.

Boc-(ACPC-*dm*-ACPC)$_2$-OBn (2) was prepared from dipeptide **10**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.4 Hz, 1H), 7.99 (d, *J* = 6.3 Hz, 1H), 7.39-7.24 (m, 5H), 7.22 (d, *J* = 8.0 Hz, 1H), 5.12 (ABq, J_{AB} = 12.6 Hz, $\Delta\upsilon$ = 0.11 ppm, 2H), 4.75 (d, *J* = 6.7 Hz, 1H), 4.58 (quintet, *J* = 8.3 Hz, 1H), 4.41 (quintet, *J* = 7.8 Hz, 1H), 4.11 (quintet, *J* = 6.2 Hz, 1H), 3.93 (quintet, *J* = 7.1 Hz, 1H), 2.97 (q, *J* = 9.0 Hz, 1H), 2.61-2.51 (m, 2H), 2.44 (q, *J* = 7.4 Hz, 1H), 2.15-1.57 (m, 16H), 1.55-1.33 (m, 4H), 1.45 (s, 9H), 1.09 (br s, 6H), 1.06 (s, 3H), 1.04 (s, 3H); ESI-TOF MS *m/*z calculated for $C_{40}H_{60}N_4O_7$ 708.4, found 709.5 $[M+H]^+$, 731.5 $[M+Na]^+$.

Boc-*ent*-ACPC-*ent*-*dm*-ACPC-*ent*-ACPC-OBn (11) was prepared from Boc-*ent*-ACPC-OH and Boc-*ent*-*dm*-ACPC-OH, both of which were synthesized by the method used for Boc-ACPC-OH and Boc-*dm*-ACPC-OH. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.39-7.24 (m, 5H), 5.12 (ABq, J_{AB} = 12.6 Hz, $\Delta\upsilon$ = 0.10 ppm, 2H), 4.76 (d, *J* = 6.5 Hz, 1H), 4.46 (quintet, *J* = 7.2 Hz, 1H), 4.35 (quintet, *J* = 7.6 Hz, 1H), 3.93 (quintet, *J* = 6.7 Hz, 1H), 2.79 (q, *J* = 7.7 Hz, 1H), 2.69 (q, *J* = 8.2 Hz, 1H), 2.54 (q, *J* = 7.3 Hz, 1H), 2.12-1.34 (m, 16H), 1.44 (s, 9H), 1.08 (s, 3H), 0.97 (s, 3H); ESI-TOF MS *m/*z calculated for $C_{32}H_{47}N_3O_6$ 569.4, found 570.4 $[M+H]^+$, 592.3 $[M+Na]^+$, 1161.7 $[2M+Na]^+$.

Boc-(*ent*-ACPC-*ent*-*dm*-ACPC)$_2$-*ent*-ACPC-OBn (3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, *J* = 7.0 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.42-7.23 (m, 5H),

6.45 (d, J = 8.4 Hz, 1H), 5.15 (ABq, J_{AB} = 12.3 Hz, $\Delta\upsilon$ = 0.12 ppm, 2H), 4.92 (d, J = 8.0 Hz, 1H), 4.57-4.34 (m, 3H), 4.25 (quintet, J = 7.5 Hz, 1H), 3.99 (quintet, J = 8.0 Hz, 1H), 3.00 (q, J = 7.1 Hz, 1H), 2.68 (q, J = 8.3 Hz, 1H), 2.48 (q, J = 8.5 Hz, 2H), 2.31 (q, J = 8.0 Hz, 1H), 2.17-1.55 (m, 22H), 1.55-1.31 (m, 4H), 1.45 (s, 9H), 1.08 (s, 3H), 1.07 (s, 3H), 1.01 (s, 3H), 1.00 (s, 3H); ESI-TOF MS *m/*z calculated for $C_{46}H_{69}N_5O_8$ 819.5, found 820.6 $[M+H]^+$, 842.5 $[M+Na]^+$.

Boc-(ACPC-*dm*-ACPC)$_3$-OBn (12). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 7.5 Hz, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 9.4 Hz, 1H), 7.59 (d, J = 9.2 Hz, 1H), 7.42-7.20 (m, 5H), 6.48 (d, J = 7.7 Hz, 1H), 5.39 (d, J = 8.7 Hz, 1H), 5.16 (ABq, J_{AB} = 12.6 Hz, $\Delta\upsilon$ = 0.15 ppm, 2H), 4.61 (quintet, J = 8.0 Hz, 1H), 4.51 (quintet, J = 8.6 Hz, 1H), 4.43 (quintet, J = 8.1 Hz, 1H), 4.35-4.16 (m, 2H), 4.02 (quintet, J = 8.6 Hz, 1H), 3.16 (q, J = 8.7 Hz, 1H), 2.73-2.54 (m, 2H), 2.44 (q, J = 7.7 Hz, 1H), 2.42 (q, J = 7.7 Hz, 1H), 2.33 (q, J = 8.5 Hz, 1H), 2.17-1.34 (m, 30H), 1.44 (s, 9H), 1.10 (s, 3H), 1.09 (s, 3H), 1.06 (s, 3H), 1.04 (br s, 6H), 0.98 (s, 3H); ESI-TOF MS *m/*z calculated for $C_{54}H_{81}N_6O_9$ 958.6, found 959.7 $[M+H]^+$, 981.7 $[M+Na]^+$.

Boc-(ACPC-*dm*-ACPC)$_4$-OBn (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59-8.44 (m, 3H), 8.40 (d, J = 9.7 Hz, 1H), 8.34 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 9.4 Hz, 1H), 7.35-7.24 (m, 5H), 6.65 (d, J = 8.1 Hz, 1H), 5.59 (d, J = 8.7 Hz, 1H), 5.11 (ABq, J_{AB} = 12.6 Hz, $\Delta\upsilon$ = 0.19 ppm, 2H), 4.58 (quintet, J = 7.6 Hz, 1H), 4.51-4.32 (m, 3H), 4.30-4.09 (m, 3H), 3.96 (quintet, J = 8.7 Hz, 1H), 3.14 (q, J = 8.7 Hz, 1H), 2.68-2.46 (m, 3H), 2.45-2.26 (m, 4H), 2.11-1.41 (m, 40H), 1.38 (s, 9H), 1.03 (br s, 6H), 1.00 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H), 0.96 (br s, 6H), 0.94 (s, 3H); ESI-TOF MS *m/*z calculated for $C_{68}H_{104}N_8O_{11}$ 1208.8, found 1232.1 $[M+Na]^+$.

Boc-ACPC-ACPC-ACPC-β^3-hPhe-ACPC-ACPC-Aib-OPBB (5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.9 Hz, 1H), 7.65 (d, J = 9.5 Hz, 1H), 7.45 (d, J = 8.6 Hz, 2H), 7.31-7.12 (m, 7H), 6.64 (d, J = 8.0 Hz, 1H),

5.53 (d, J = 9.1 Hz, 1H), 5.08 (ABq, J_{AB} = 12.7 Hz, $\Delta\upsilon$ = 0.11 ppm, 2H), 4.44 (quintet, J = 7.2 Hz, 1H), 4.37-4.15 (m, 4H), 4.08 (quintet, J = 8.6 Hz, 1H), 2.83 (d, J = 8.0 Hz, 2H), 2.76 (q, J = 7.3 Hz, 1H), 2.53-2.14 (m, 6H), 2.14-1.49 (m, 30H), 1.55 (s, 3H), 1.47 (s, 3H), 1.44 (s, 9H); ESI-TOF MS *m/*z calculated for $C_{56}H_{78}BrN_7O_{10}$ 1087.5, 1089.5, found 1088.9, 1090.9 $[M+H]^+$, 1110.9, 1112.9 $[M+Na]^+$.

Crystallization and X-ray analysis

X-ray quality crystals were grown from various solvent mixtures by slow evaporation or solvent diffusion (Table S1).

Table S1. Crystallization conditions and deposition numbers.

CCDC number[a]	β-peptide	crystallization condition (solvent mixture)
708632	**1**	Solvent diffusion (*n*-pentane/Et_2O/$CHCl_3$)
708634	**2**	Solvent diffusion (*n*-pentane/Et_2O/$CHCl_3$)
708631	**3**	Solvent diffusion (*n*-pentane/Et_2O/$CHCl_3$)
708633	**4**	Solvent diffusion (*n*-heptane/DCE)
n/a[b]	**5**	Slow evaporation (MeOH/H_2O)
708637	**5**	Slow evaporation (^{i}PrOH)

a. Deposition number at the Cambridge Crystallographic Data Centre (CCDC).
b. The crystal data was not deposited because of low resolution.

General procedure for crystallization

Glass vials (1 dram, 4 mL) were washed with acetone and dried under a nitrogen gas stream before use. White polypropylene caps with a Teflon liner were used. β-Peptides were purified carefully by column chromatography before crystallization was undertaken. HPLC-grade solvents were used. All crystallization attempts were conducted at room temperature.

Crystallization from an n-pentane/ether/chloroform mixture (**1**,**2**, and **3**)

To a glass vial charged with a β-peptide (10-20 mg), chloroform (0.2-0.4 mL) was added dropwise until the β-peptide was completely dissolved. Ether (0.4-0.6 mL) was then added. The mixture was gently shaken. A few drops of n-pentane were added with gentle shaking of the vial. The vial was closed with a cap. A few more drops of n-pentane were added if no crystal had appeared after 12 h.

Crystallization from an n-heptane/dichloroethane mixture (**4**)

To a glass vial charged with β-peptide **4** (10-20 mg), dichloroethane (0.6-1.0 mL) was added dropwise until the β-peptide was completely dissolved. A few drops of n-heptane were added with gentle shaking of the vial. The vial was closed with a cap. A few more drops of n-heptane were added if no crystal had appeared after 12 h.

Slow evaporation of a methanol/water mixture (**5**)

β-Peptide **5** (10-20 mg) was dissolved in methanol (1-2 mL). The solution was transferred through a syringe filter into a glass vial with a screw cap. A few drops of water were added. The vial was closed with a cap, and then shaken gently until the turbid mixture turned clear. The cap was slightly unscrewed to let the solvent mixture evaporate slowly. High-quality crystals were obtained after a few days, before the sample was completely dry.

Slow evaporation of an isopropanol solution (**5**)

β-Peptide **5** (10-20 mg) was dissolved in isopropanol (1-2 mL). The solution was transferred through a syringe filter into a glass vial with a screw cap. The cap was slightly unscrewed to let the solvent evaporate slowly. High-quality crystals were obtained after two or three weeks.

Table S2. Helical parameters calculated from sets of four consecutive α-carbons.

β-peptide	res/turn *n*	rise/turn *p* (Å)	rise/res *d* (Å)	radius *r* (Å)
3	2.6	5.6	2.1	2.1
Boc-$(ACPC)_6$-OBn[a]	2.5	5.1	2.1	1.9
	2.5	5.3	2.1	2.0
Boc-$(ACPC)_8$-OBn[a]	2.7	5.3	2.0	2.2
	2.7	5.5	2.1	2.1
	2.7	5.5	2.0	2.2
	2.8	5.2	1.9	2.3
4	2.8	5.4	2.0	2.2
	2.7	5.5	2.0	2.2
	2.7	5.5	2.0	2.2
	2.7	5.3	2.0	2.2
5	2.8	5.5	2.0	2.2
	2.8	5.3	1.9	2.2
	2.7	5.3	2.0	2.1
average	**2.7**	**5.4**	**2.0**	**2.1**

a. reference 5c of the main text

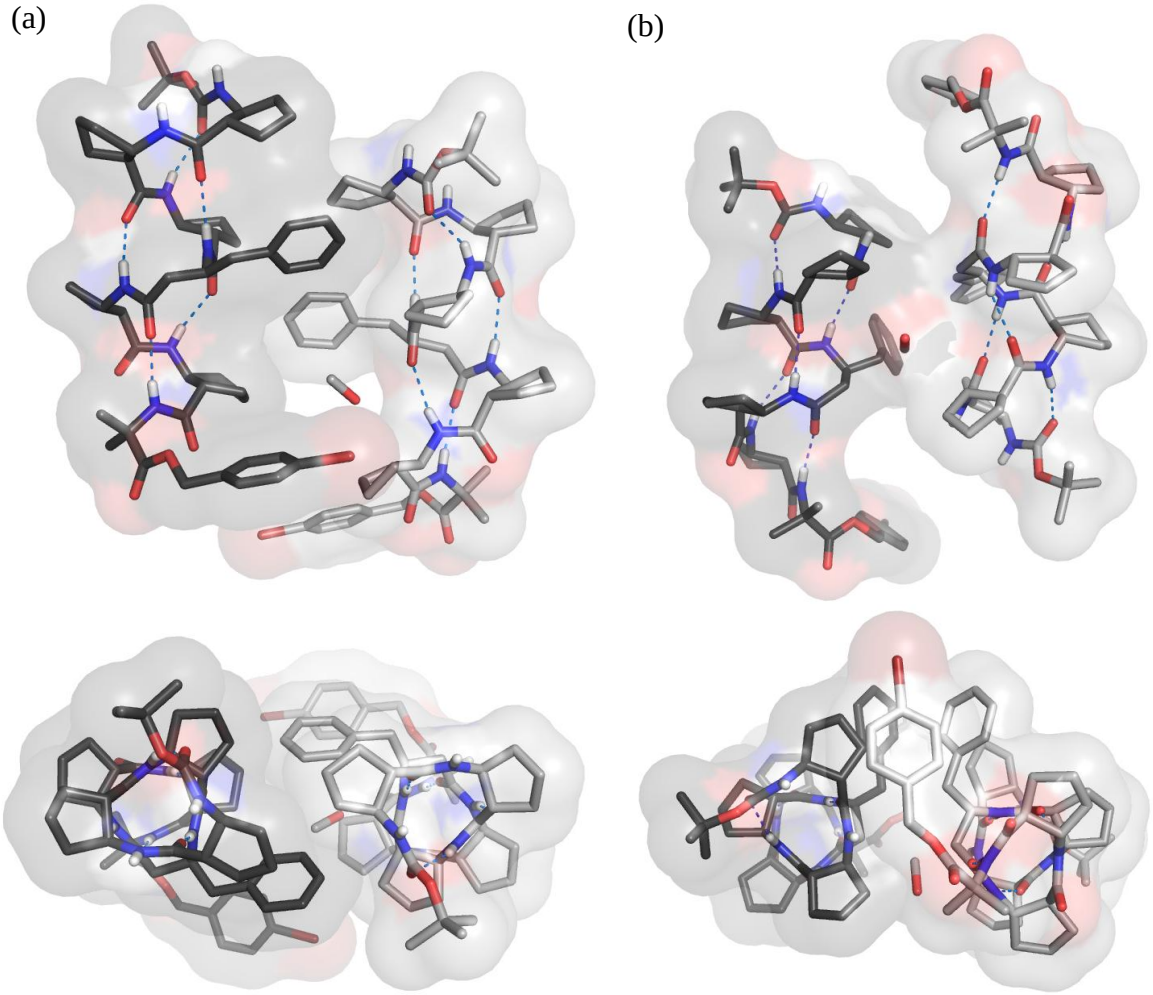


Figure S1. Crystal structure of heptamer **5** co-crystallized with methanol: (a) close packing of two independent molecules that display parallel orientation, viewed along the crystallographic *b* axis (top) and *a* axis (bottom), (b) close packing between independent molecules that display antiparallel orientation, viewed along the crystallographic *c* axis (top) and *a* axis (bottom). Disordered solvent molecules and most hydrogen atoms are omitted for clarity. Molecular surfaces for the helical conformations are rendered as shaded areas.

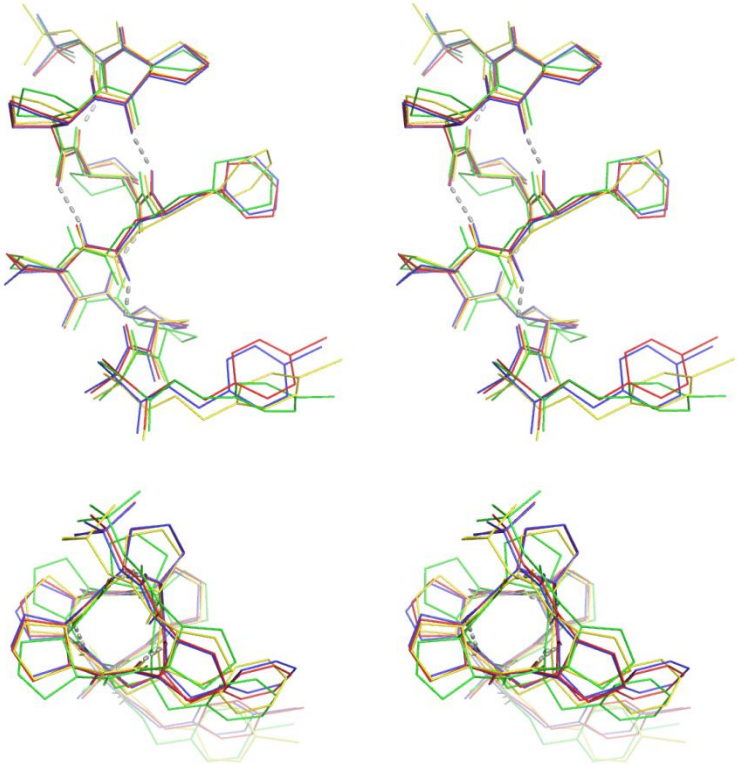


Figure S2. Overay of four symmetry-independent conformations observed in the crystals of heptamer **5** that were grown under two solvent conditions (stereoview). Dotted lines indicate intramolecular hydrogen bonds.

Crystal Structure Report

Boc-(dm-ACPC)$_4$-OBn (1)

Data Collection

A colorless crystal with approximate dimensions 0.6 x 0.4 x 0.4 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. A total of 321 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 36933 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.71 Å. A total of 83765 data were harvested by collecting four sets of frames with 0.3º scans in ω and one set with 0.45º scans in φ with an exposure time 20 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement [S1].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic

displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. There is one molecule of foldamer and one molecule of chloroform in the asymmetric unit.

The final least-squares refinement of 491 parameters against 13037 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0348 and 0.0944, respectively. The final difference Fourier map was featureless.

Table S3. Crystal data and structure refinement for β-peptide tetramer **1**

Empirical formula	$C_{39}\ H_{65}\ Cl_3\ N_4\ O_7$	
Formula weight	808.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.5593(2) Å	α= 90°.
	b = 18.8150(4) Å	β= 90°.
	c = 22.6797(5) Å	γ = 90°.
Volume	4505.85(16) $Å^3$	
Z	4	
Density (calculated)	1.192 Mg/m^3	
Absorption coefficient	0.251 mm^{-1}	
F(000)	1736	
Crystal size	0.60 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.80 to 30.07°.	
Index ranges	-14<=h<=14, -26<=k<=26, -31<=l<=31	
Reflections collected	83765	
Independent reflections	13037 [R(int) = 0.0298]	
Completeness to theta = 30.07°	99.3 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9062 and 0.8639	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13037 / 0 / 491	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0348, wR2 = 0.0869	
R indices (all data)	R1 = 0.0420, wR2 = 0.0944	
Absolute structure parameter	-0.06(3)	
Largest diff. peak and hole	0.411 and -0.213 $e.Å^{-3}$	

Table S4. Torsion angles [°] for **1**

C(5)-O(1)-C(4)-C(2)	-172.16(12)	C(14)-C(20)-C(21)-O(4)	77.39(15)
C(5)-O(1)-C(4)-C(1)	69.94(15)	C(19)-C(20)-C(21)-N(3)	139.10(11)
C(5)-O(1)-C(4)-C(3)	-54.94(15)	C(14)-C(20)-C(21)-N(3)	-103.08(12)
C(6)-N(1)-C(5)-O(2)	-1.2(2)	C(21)-N(3)-C(22)-C(23)	93.73(13)
C(6)-N(1)-C(5)-O(1)	178.39(11)	C(21)-N(3)-C(22)-C(28)	-147.17(11)
C(4)-O(1)-C(5)-O(2)	-15.44(19)	N(3)-C(22)-C(23)-C(24)	115.27(11)
C(4)-O(1)-C(5)-N(1)	164.94(11)	C(28)-C(22)-C(23)-C(24)	-7.13(13)
C(5)-N(1)-C(6)-C(7)	138.23(12)	C(22)-C(23)-C(24)-C(26)	148.07(11)
C(5)-N(1)-C(6)-C(12)	-105.89(13)	C(22)-C(23)-C(24)-C(25)	-88.97(13)
N(1)-C(6)-C(7)-C(8)	164.78(10)	C(22)-C(23)-C(24)-C(27)	28.97(13)
C(12)-C(6)-C(7)-C(8)	41.90(12)	C(26)-C(24)-C(27)-C(28)	-159.70(12)
C(6)-C(7)-C(8)-C(9)	-144.79(11)	C(25)-C(24)-C(27)-C(28)	76.95(15)
C(6)-C(7)-C(8)-C(10)	93.44(14)	C(23)-C(24)-C(27)-C(28)	-40.50(13)
C(6)-C(7)-C(8)-C(11)	-23.87(13)	C(24)-C(27)-C(28)-C(29)	158.19(11)
C(9)-C(8)-C(11)-C(12)	116.59(12)	C(24)-C(27)-C(28)-C(22)	36.61(13)
C(10)-C(8)-C(11)-C(12)	-121.50(12)	N(3)-C(22)-C(28)-C(29)	95.36(11)
C(7)-C(8)-C(11)-C(12)	-3.35(13)	C(23)-C(22)-C(28)-C(29)	-140.58(10)
C(8)-C(11)-C(12)-C(13)	148.33(10)	N(3)-C(22)-C(28)-C(27)	-141.92(10)
C(8)-C(11)-C(12)-C(6)	28.74(13)	C(23)-C(22)-C(28)-C(27)	-17.86(12)
N(1)-C(6)-C(12)-C(13)	71.79(12)	C(30)-N(4)-C(29)-O(5)	-0.6(2)
C(7)-C(6)-C(12)-C(13)	-165.82(10)	C(30)-N(4)-C(29)-C(28)	178.53(12)
N(1)-C(6)-C(12)-C(11)	-165.69(10)	C(27)-C(28)-C(29)-O(5)	-8.71(17)
C(7)-C(6)-C(12)-C(11)	-43.30(12)	C(22)-C(28)-C(29)-O(5)	108.64(13)
C(14)-N(2)-C(13)-O(3)	-2.72(19)	C(27)-C(28)-C(29)-N(4)	172.13(12)
C(14)-N(2)-C(13)-C(12)	173.41(10)	C(22)-C(28)-C(29)-N(4)	-70.52(14)
C(11)-C(12)-C(13)-O(3)	-43.14(16)	C(29)-N(4)-C(30)-C(31)	105.38(15)
C(6)-C(12)-C(13)-O(3)	71.97(14)	C(29)-N(4)-C(30)-C(36)	-135.75(13)
C(11)-C(12)-C(13)-N(2)	140.66(11)	N(4)-C(30)-C(31)-C(32)	153.40(12)
C(6)-C(12)-C(13)-N(2)	-104.23(12)	C(36)-C(30)-C(31)-C(32)	30.01(14)
C(13)-N(2)-C(14)-C(15)	158.43(11)	C(30)-C(31)-C(32)-C(34)	73.84(16)
C(13)-N(2)-C(14)-C(20)	-84.91(13)	C(30)-C(31)-C(32)-C(33)	-162.67(16)
N(2)-C(14)-C(15)-C(16)	101.30(11)	C(30)-C(31)-C(32)-C(35)	-43.01(14)
C(20)-C(14)-C(15)-C(16)	-19.56(12)	C(34)-C(32)-C(35)-C(36)	-77.15(15)
C(14)-C(15)-C(16)-C(18)	156.39(10)	C(33)-C(32)-C(35)-C(36)	159.43(14)
C(14)-C(15)-C(16)-C(17)	-80.30(12)	C(31)-C(32)-C(35)-C(36)	39.62(15)
C(14)-C(15)-C(16)-C(19)	37.24(12)	C(32)-C(35)-C(36)-C(37)	101.76(14)
C(18)-C(16)-C(19)-C(20)	-160.48(11)	C(32)-C(35)-C(36)-C(30)	-21.75(14)
C(17)-C(16)-C(19)-C(20)	77.60(12)	N(4)-C(30)-C(36)-C(37)	104.82(13)
C(15)-C(16)-C(19)-C(20)	-41.07(12)	C(31)-C(30)-C(36)-C(37)	-131.64(12)
C(16)-C(19)-C(20)-C(21)	152.02(10)	N(4)-C(30)-C(36)-C(35)	-128.49(12)
C(16)-C(19)-C(20)-C(14)	29.72(12)	C(31)-C(30)-C(36)-C(35)	-4.95(14)
N(2)-C(14)-C(20)-C(21)	111.72(11)	C(38)-O(7)-C(37)-O(6)	0.4(2)
C(15)-C(14)-C(20)-C(21)	-127.96(10)	C(38)-O(7)-C(37)-C(36)	178.02(16)
N(2)-C(14)-C(20)-C(19)	-126.51(10)	C(35)-C(36)-C(37)-O(6)	-151.62(14)
C(15)-C(14)-C(20)-C(19)	-6.19(11)	C(30)-C(36)-C(37)-O(6)	-31.01(19)
C(22)-N(3)-C(21)-O(4)	0.36(18)	C(35)-C(36)-C(37)-O(7)	30.78(17)
C(22)-N(3)-C(21)-C(20)	-179.17(10)	C(30)-C(36)-C(37)-O(7)	151.40(12)
C(19)-C(20)-C(21)-O(4)	-40.44(16)		

Symmetry transformations used to generate equivalent atoms:

Table S5. Hydrogen bonds for **1**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(6)#1	0.88	2.08	2.9564(15)	171.6
N(2)-H(2)...O(5)#1	0.88	1.94	2.8183(13)	171.6
N(3)-H(3)...O(2)	0.88	2.09	2.9678(13)	174.6
N(4)-H(4)...O(3)	0.88	2.00	2.7970(14)	150.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+1/2

Boc-(ACPC-dm-ACPC)$_2$-OBn (2)

Data Collection

A colorless crystal with approximate dimensions 0.43 x 0.09 x 0.08 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 105(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. A total of 90 reflections was obtained. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 4756 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.73 Å. A total of 17224 data were harvested by collecting four sets of frames with 0.36º scans in ω and one set with 0.45º scans in φ with an exposure time 60 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P\bar{1}$ and *P*1. The *E*-statistics strongly suggested the centrosymmetric space group *P*1 that yielded chemically reasonable and computationally stable results of refinement [S1].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation

at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 467 parameters against 5316 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0513 and 0.1294, respectively. The final difference Fourier map was featureless.

Table S6. Crystal data and structure refinement for β-peptide tetramer **2**

Empirical formula	$C_{40}\ H_{60}\ N_4\ O_7$	
Formula weight	708.92	
Temperature	105(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.491(3) Å	α= 94.225(5)°.
	b = 9.624(3) Å	β= 93.287(5)°.
	c = 11.899(4) Å	γ = 112.310(5)°.
Volume	998.5(5) $Å^3$	
Z	1	
Density (calculated)	1.179 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	384	
Crystal size	0.43 x 0.09 x 0.08 mm^3	
Theta range for data collection	2.33 to 29.34°.	
Index ranges	-12<=h<=12, -12<=k<=13, -16<=l<=16	
Reflections collected	17224	
Independent reflections	5316 [R(int) = 0.0417]	
Completeness to theta = 29.34°	97.0 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9936 and 0.9662	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5316 / 3 / 467	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1215	
R indices (all data)	R1 = 0.0650, wR2 = 0.1294	
Absolute structure parameter	Not reliable [0.7(10)]	
Largest diff. peak and hole	0.482 and -0.210 $e.Å^{-3}$	

Table S7. Torsion angles [°] for **2**

C(5)-O(1)-C(4)-C(3)	-65.6(3)	N(3)-C(20)-C(21)-C(22)	154.1(3)
C(5)-O(1)-C(4)-C(2)	59.4(4)	C(24)-C(20)-C(21)-C(22)	32.4(3)
C(5)-O(1)-C(4)-C(1)	176.0(3)	C(20)-C(21)-C(22)-C(23)	-41.4(3)
C(6)-N(1)-C(5)-O(2)	-1.8(4)	C(21)-C(22)-C(23)-C(24)	34.5(3)
C(6)-N(1)-C(5)-O(1)	177.7(2)	C(22)-C(23)-C(24)-C(25)	104.7(3)
C(4)-O(1)-C(5)-O(2)	-6.6(4)	C(22)-C(23)-C(24)-C(20)	-14.3(3)
C(4)-O(1)-C(5)-N(1)	173.9(3)	N(3)-C(20)-C(24)-C(25)	103.9(2)
C(5)-N(1)-C(6)-C(7)	151.5(3)	C(21)-C(20)-C(24)-C(25)	-133.0(2)
C(5)-N(1)-C(6)-C(10)	-90.4(3)	N(3)-C(20)-C(24)-C(23)	-134.1(2)
N(1)-C(6)-C(7)-C(8)	162.6(3)	C(21)-C(20)-C(24)-C(23)	-11.0(3)
C(10)-C(6)-C(7)-C(8)	38.9(3)	C(26)-N(4)-C(25)-O(5)	-10.4(4)
C(6)-C(7)-C(8)-C(9)	-37.8(3)	C(26)-N(4)-C(25)-C(24)	167.1(2)
C(7)-C(8)-C(9)-C(10)	21.8(4)	C(23)-C(24)-C(25)-O(5)	-16.1(3)
C(8)-C(9)-C(10)-C(11)	122.8(3)	C(20)-C(24)-C(25)-O(5)	101.1(3)
C(8)-C(9)-C(10)-C(6)	2.6(3)	C(23)-C(24)-C(25)-N(4)	166.4(2)
N(1)-C(6)-C(10)-C(11)	90.2(3)	C(20)-C(24)-C(25)-N(4)	-76.4(3)
C(7)-C(6)-C(10)-C(11)	-147.0(2)	C(25)-N(4)-C(26)-C(27)	-62.1(3)
N(1)-C(6)-C(10)-C(9)	-148.4(2)	C(25)-N(4)-C(26)-C(32)	59.4(3)
C(7)-C(6)-C(10)-C(9)	-25.5(3)	N(4)-C(26)-C(27)-C(28)	155.1(2)
C(12)-N(2)-C(11)-O(3)	-4.9(4)	C(32)-C(26)-C(27)-C(28)	28.4(3)
C(12)-N(2)-C(11)-C(10)	176.1(2)	C(26)-C(27)-C(28)-C(29)	-159.4(2)
C(9)-C(10)-C(11)-O(3)	-58.9(3)	C(26)-C(27)-C(28)-C(30)	77.9(3)
C(6)-C(10)-C(11)-O(3)	57.8(3)	C(26)-C(27)-C(28)-C(31)	-40.4(3)
C(9)-C(10)-C(11)-N(2)	120.2(3)	C(29)-C(28)-C(31)-C(32)	156.7(2)
C(6)-C(10)-C(11)-N(2)	-123.1(2)	C(30)-C(28)-C(31)-C(32)	-81.1(3)
C(11)-N(2)-C(12)-C(13)	166.1(2)	C(27)-C(28)-C(31)-C(32)	37.0(3)
C(11)-N(2)-C(12)-C(18)	-77.4(3)	N(4)-C(26)-C(32)-C(33)	106.8(2)
N(2)-C(12)-C(13)-C(14)	158.6(2)	C(27)-C(26)-C(32)-C(33)	-127.3(2)
C(18)-C(12)-C(13)-C(14)	36.9(3)	N(4)-C(26)-C(32)-C(31)	-131.0(2)
C(12)-C(13)-C(14)-C(16)	-159.5(2)	C(27)-C(26)-C(32)-C(31)	-5.1(3)
C(12)-C(13)-C(14)-C(15)	77.4(3)	C(28)-C(31)-C(32)-C(33)	102.8(3)
C(12)-C(13)-C(14)-C(17)	-40.7(3)	C(28)-C(31)-C(32)-C(26)	-20.0(3)
C(13)-C(14)-C(17)-C(18)	28.9(3)	C(34)-O(7)-C(33)-O(6)	2.2(4)
C(16)-C(14)-C(17)-C(18)	148.6(2)	C(34)-O(7)-C(33)-C(32)	-175.8(2)
C(15)-C(14)-C(17)-C(18)	-88.3(3)	C(26)-C(32)-C(33)-O(6)	8.0(4)
C(14)-C(17)-C(18)-C(19)	115.7(2)	C(31)-C(32)-C(33)-O(6)	-110.7(3)
C(14)-C(17)-C(18)-C(12)	-6.9(3)	C(26)-C(32)-C(33)-O(7)	-174.0(2)
N(2)-C(12)-C(18)-C(19)	99.4(2)	C(31)-C(32)-C(33)-O(7)	67.3(3)
C(13)-C(12)-C(18)-C(19)	-139.8(2)	C(33)-O(7)-C(34)-C(35)	-147.2(3)
N(2)-C(12)-C(18)-C(17)	-138.9(2)	O(7)-C(34)-C(35)-C(36)	21.4(4)
C(13)-C(12)-C(18)-C(17)	-18.0(2)	O(7)-C(34)-C(35)-C(40)	-163.2(3)
C(20)-N(3)-C(19)-O(4)	1.2(4)	C(40)-C(35)-C(36)-C(37)	-0.7(4)
C(20)-N(3)-C(19)-C(18)	-177.5(2)	C(34)-C(35)-C(36)-C(37)	174.6(3)
C(17)-C(18)-C(19)-O(4)	-53.6(3)	C(35)-C(36)-C(37)-C(38)	0.0(5)
C(12)-C(18)-C(19)-O(4)	64.6(3)	C(36)-C(37)-C(38)-C(39)	0.7(5)
C(17)-C(18)-C(19)-N(3)	125.0(2)	C(37)-C(38)-C(39)-C(40)	-0.8(5)
C(12)-C(18)-C(19)-N(3)	-116.8(2)	C(38)-C(39)-C(40)-C(35)	0.2(5)
C(19)-N(3)-C(20)-C(21)	102.3(3)	C(36)-C(35)-C(40)-C(39)	0.6(4)
C(19)-N(3)-C(20)-C(24)	-139.4(2)	C(34)-C(35)-C(40)-C(39)	-175.0(3)

Symmetry transformations used to generate equivalent atoms:

Table S8. Hydrogen bonds for **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(4)#1	0.88	2.08	2.910(3)	157.4
N(2)-H(2)...O(5)#2	0.88	1.95	2.824(3)	170.5
N(3)-H(3)...O(2)	0.88	2.07	2.890(3)	155.6
N(4)-H(4)...O(3)	0.88	2.06	2.796(3)	140.3

Symmetry transformations used to generate equivalent atoms:
#1 x+1,y,z #2 x,y-1,z

Boc-(ent-ACPC-ent-dm-ACPC)$_2$-ent-ACPC-OBn (3)

Data Collection

A colorless crystal with approximate dimensions 0.51 x 0.48 x 0.10 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 105(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 9293 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.73 Å. A total of 20594 data were harvested by collecting three sets of frames with 0.3º scans in ω and one set with 0.45º scans in φ with an exposure time 60 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space group $P2_1$that yielded chemically reasonable and computationally stable results of refinement [S1].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms except C8 were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Atom C8 is equally disordered over two positions and was refined isotropically. There is also a solvent molecule of Et2O per foldamer in the lattice. Two atoms in the solvent, C49 and O9 are disordered in a 0.652(6):0.348(6) ratio over two positions. Some restraints have been applies.

The final least-squares refinement of 591 parameters against 6686 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0623 and 0.1627, respectively. The final difference Fourier map was featureless.

Table S9. Crystal data and structure refinement for β-peptide pentamer **3**

Empirical formula	$C_{50}\ H_{79}\ N_5\ O_9$	
Formula weight	894.18	
Temperature	105(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.446(2) Å	α= 90°.
	b = 19.955(4) Å	β= 95.020(3)°.
	c = 12.161(2) Å	γ = 90°.
Volume	2525.1(9) $Å^3$	
Z	2	
Density (calculated)	1.176 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	972	
Crystal size	0.51 x 0.48 x 0.10 mm^3	
Theta range for data collection	1.97 to 28.70°.	
Index ranges	-13<=h<=14, -26<=k<=26, -16<=l<=16	
Reflections collected	34109	
Independent reflections	6686 [R(int) = 0.0621]	
Completeness to theta = 28.70°	99.7 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.9920 and 0.9602	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6686 / 11 / 591	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0623, wR2 = 0.1509	
R indices (all data)	R1 = 0.0841, wR2 = 0.1627	
Absolute structure parameter	Not reliable [0.8(12)]	
Largest diff. peak and hole	0.374 and -0.527 $e.Å^{-3}$	

Table S10. Torsion angles [°] for **3**

C(5)-O(1)-C(4)-C(1)	-64.9(4)	C(13)-C(12)-C(18)-C(19)	137.4(3)
C(5)-O(1)-C(4)-C(2)	59.7(5)	N(2)-C(12)-C(18)-C(17)	137.0(3)
C(5)-O(1)-C(4)-C(3)	177.3(3)	C(13)-C(12)-C(18)-C(17)	14.9(3)
C(6)-N(1)-C(5)-O(2)	-1.8(6)	C(20)-N(3)-C(19)-O(4)	2.9(5)
C(6)-N(1)-C(5)-O(1)	178.1(3)	C(20)-N(3)-C(19)-C(18)	-175.7(3)
C(4)-O(1)-C(5)-O(2)	9.6(5)	C(17)-C(18)-C(19)-O(4)	30.6(4)
C(4)-O(1)-C(5)-N(1)	-170.4(3)	C(12)-C(18)-C(19)-O(4)	-87.2(3)
C(5)-N(1)-C(6)-C(10)	101.7(4)	C(17)-C(18)-C(19)-N(3)	-150.7(3)
C(5)-N(1)-C(6)-C(7)	-140.9(4)	C(12)-C(18)-C(19)-N(3)	91.5(3)
N(1)-C(6)-C(7)-C(8)	-155.8(4)	C(19)-N(3)-C(20)-C(21)	-127.1(3)
C(10)-C(6)-C(7)-C(8)	-32.8(5)	C(19)-N(3)-C(20)-C(24)	113.1(3)
N(1)-C(6)-C(7)-C(8A)	-129.8(5)	N(3)-C(20)-C(21)-C(22)	-160.9(3)
C(10)-C(6)-C(7)-C(8A)	-6.8(5)	C(24)-C(20)-C(21)-C(22)	-36.2(4)
C(8A)-C(7)-C(8)-C(9)	-75.3(6)	C(20)-C(21)-C(22)-C(23)	43.2(4)
C(6)-C(7)-C(8)-C(9)	20.2(6)	C(21)-C(22)-C(23)-C(24)	-33.5(4)
C(8)-C(7)-C(8A)-C(9)	71.2(6)	C(22)-C(23)-C(24)-C(25)	-106.9(4)
C(6)-C(7)-C(8A)-C(9)	-20.8(6)	C(22)-C(23)-C(24)-C(20)	10.7(4)
C(7)-C(8)-C(9)-C(10)	0.1(7)	N(3)-C(20)-C(24)-C(25)	-98.5(3)
C(7)-C(8)-C(9)-C(8A)	74.7(6)	C(21)-C(20)-C(24)-C(25)	136.7(3)
C(7)-C(8A)-C(9)-C(8)	-71.8(6)	N(3)-C(20)-C(24)-C(23)	140.8(3)
C(7)-C(8A)-C(9)-C(10)	39.8(6)	C(21)-C(20)-C(24)-C(23)	16.0(4)
N(1)-C(6)-C(10)-C(11)	-84.8(3)	C(26)-N(4)-C(25)-O(5)	5.7(5)
C(7)-C(6)-C(10)-C(11)	153.8(3)	C(26)-N(4)-C(25)-C(24)	-171.9(3)
N(1)-C(6)-C(10)-C(9)	153.3(3)	C(23)-C(24)-C(25)-O(5)	27.3(5)
C(7)-C(6)-C(10)-C(9)	31.9(4)	C(20)-C(24)-C(25)-O(5)	-88.6(4)
C(8)-C(9)-C(10)-C(11)	-141.5(4)	C(23)-C(24)-C(25)-N(4)	-155.0(3)
C(8A)-C(9)-C(10)-C(11)	-165.8(4)	C(20)-C(24)-C(25)-N(4)	89.0(4)
C(8)-C(9)-C(10)-C(6)	-20.1(5)	C(25)-N(4)-C(26)-C(27)	-141.1(3)
C(8A)-C(9)-C(10)-C(6)	-44.4(4)	C(25)-N(4)-C(26)-C(32)	98.7(4)
C(12)-N(2)-C(11)-O(3)	-0.2(5)	N(4)-C(26)-C(27)-C(28)	-122.4(3)
C(12)-N(2)-C(11)-C(10)	-178.9(3)	C(32)-C(26)-C(27)-C(28)	1.8(4)
C(6)-C(10)-C(11)-O(3)	-63.0(4)	C(26)-C(27)-C(28)-C(29)	93.3(4)
C(9)-C(10)-C(11)-O(3)	53.6(4)	C(26)-C(27)-C(28)-C(30)	-144.8(3)
C(6)-C(10)-C(11)-N(2)	115.7(3)	C(26)-C(27)-C(28)-C(31)	-24.9(4)
C(9)-C(10)-C(11)-N(2)	-127.7(3)	C(29)-C(28)-C(31)-C(32)	-79.1(4)
C(11)-N(2)-C(12)-C(13)	-144.1(3)	C(30)-C(28)-C(31)-C(32)	159.2(3)
C(11)-N(2)-C(12)-C(18)	97.3(4)	C(27)-C(28)-C(31)-C(32)	39.2(3)
N(2)-C(12)-C(13)-C(14)	-158.4(3)	C(28)-C(31)-C(32)-C(33)	-161.7(3)
C(18)-C(12)-C(13)-C(14)	-34.2(3)	C(28)-C(31)-C(32)-C(26)	-38.6(3)
C(12)-C(13)-C(14)-C(15)	159.4(3)	N(4)-C(26)-C(32)-C(31)	147.2(3)
C(12)-C(13)-C(14)-C(16)	-79.3(3)	C(27)-C(26)-C(32)-C(31)	22.3(3)
C(12)-C(13)-C(14)-C(17)	39.4(3)	N(4)-C(26)-C(32)-C(33)	-90.7(3)
C(15)-C(14)-C(17)-C(18)	-149.8(3)	C(27)-C(26)-C(32)-C(33)	144.4(3)
C(13)-C(14)-C(17)-C(18)	-29.8(3)	C(34)-N(5)-C(33)-O(6)	-6.6(5)
C(16)-C(14)-C(17)-C(18)	88.2(3)	C(34)-N(5)-C(33)-C(32)	172.2(3)
C(14)-C(17)-C(18)-C(19)	-111.0(3)	C(31)-C(32)-C(33)-O(6)	40.4(4)
C(14)-C(17)-C(18)-C(12)	9.3(3)	C(26)-C(32)-C(33)-O(6)	-76.8(4)
N(2)-C(12)-C(18)-C(19)	-100.4(3)	C(31)-C(32)-C(33)-N(5)	-138.4(3)

C(26)-C(32)-C(33)-N(5)	104.4(3)	C(39)-O(8)-C(40)-C(41)	155.7(3)
C(33)-N(5)-C(34)-C(35)	-78.3(4)	O(8)-C(40)-C(41)-C(42)	5.5(5)
C(33)-N(5)-C(34)-C(38)	169.6(3)	O(8)-C(40)-C(41)-C(46)	-174.0(3)
N(5)-C(34)-C(35)-C(36)	-75.2(3)	C(46)-C(41)-C(42)-C(43)	-0.8(5)
C(38)-C(34)-C(35)-C(36)	40.5(3)	C(40)-C(41)-C(42)-C(43)	179.7(3)
C(34)-C(35)-C(36)-C(37)	-28.2(4)	C(41)-C(42)-C(43)-C(44)	-0.2(6)
C(35)-C(36)-C(37)-C(38)	4.8(4)	C(42)-C(43)-C(44)-C(45)	0.9(6)
N(5)-C(34)-C(38)-C(39)	-161.1(3)	C(43)-C(44)-C(45)-C(46)	-0.6(6)
C(35)-C(34)-C(38)-C(39)	82.0(3)	C(44)-C(45)-C(46)-C(41)	-0.4(6)
N(5)-C(34)-C(38)-C(37)	79.8(3)	C(42)-C(41)-C(46)-C(45)	1.1(6)
C(35)-C(34)-C(38)-C(37)	-37.1(3)	C(40)-C(41)-C(46)-C(45)	-179.3(4)
C(36)-C(37)-C(38)-C(39)	-98.9(3)	C(47)-C(48)-O(9)-C(49)	-170.5(6)
C(36)-C(37)-C(38)-C(34)	19.9(3)	O(9A)-C(48)-O(9)-C(49)	40.6(8)
C(40)-O(8)-C(39)-O(7)	-3.6(5)	C(48)-O(9)-C(49)-C(50)	-171.1(6)
C(40)-O(8)-C(39)-C(38)	174.6(3)	C(47)-C(48)-O(9A)-C(49A)	-77.8(13)
C(34)-C(38)-C(39)-O(7)	-14.0(5)	O(9)-C(48)-O(9A)-C(49A)	-33.0(9)
C(37)-C(38)-C(39)-O(7)	101.0(4)	C(48)-O(9A)-C(49A)-C(50)	173.9(10)
C(34)-C(38)-C(39)-O(8)	167.9(3)	O(9)-C(49)-C(50)-C(49A)	-38.8(15)
C(37)-C(38)-C(39)-O(8)	-77.2(4)	O(9A)-C(49A)-C(50)-C(49)	41.8(12)

Symmetry transformations used to generate equivalent atoms:

Table S11. Hydrogen bonds for **3** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(5)#1	0.88	2.02	2.870(4)	161.5
N(2)-H(2)...O(6)#1	0.88	2.05	2.879(4)	157.3
N(3)-H(3)...O(2)	0.88	2.08	2.900(4)	154.6
N(4)-H(4)...O(3)	0.88	2.03	2.907(4)	177.7
N(5)-H(5)...O(4)	0.88	1.92	2.795(4)	173.9

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z

Boc-(ACPC-dm-ACPC)$_4$-OBn (4)

Data Collection

A colorless crystal with approximate dimensions 0.58 x 0.21 x 0.21 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 105(2) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker CCD-1000 diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.9 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20 frames collected at intervals of 0.3º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 9892 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.8 Å. A total of 58181 data were harvested by collecting three sets of frames with 0.3º scans in ω and one set with 0.3º scans in φ with an exposure time 60 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S2]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement [S2].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms except the phenyl ring were refined with anisotropic displacement coefficients. The phenyl ring and atoms O11 and C62 were disordered over two positions in a 70.6:29.4 ratio. The disordered phenyl rings were refined isotropically and in idealized geometries. Several atoms in the five-membered rings were

disordered over two positions and refined with restraints. Atom C8 was disordered over two positions in a 66.9:33.1 ratio. Atom C22 was disordered over two positions in a 70.6:29.4 ratio. Atom C36 was disordered over two positions in a 91.8:8.2 ratio. Atom C50 was disordered over two positions in a 64.1:35.9 ratio. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Each foldamer participates in eight N-H···O hydrogen bonds. Six of the hydrogen bonds are intramolecular and two are intermolecular. All chiral carbon atoms have the absolute configuration of S determined from the synthetic procedure.

There were several partially occupied molecules of some solvent also present in the asymmetric unit. A significant amount of time was invested in identifying and refining the disordered molecules. Bond length restraints were applied to model the molecules but the resulting isotropic displacement coefficients suggested the molecules were mobile. In addition, the refinement was computationally unstable. Option SQUEEZE of program PLATON [3] was used to correct the diffraction data for diffuse scattering effects and to identify the solvate molecule. PLATON calculated the upper limit of volume that can be occupied by the solvent to be 2424 $Å^3$, or 29% of the unit cell volume. The program calculated 816 electrons in the unit cell for the diffuse species. This approximately corresponds to four molecules of dichloroethane in the asymmetric unit (50 electrons). It is very likely that these solvate molecules are disordered over several positions. Please note there is no certainty as to the composition of the solvent molecules nor their number and that all derived results in the following tables are based on the known contents. No data are given for the diffusely scattering species.

The final least-squares refinement of 790 parameters against 8795 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0993 and 0.02656, respectively. The final difference Fourier map was featureless.

Table S12. Crystal data and structure refinement for β-peptide octamer **4**

Empirical formula	$C_{68}H_{104}N_8O_{11}$	
Formula weight	1209.59	
Temperature	105(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.6925(13) Å	α= 90°.
	b = 25.843(3) Å	β= 90°.
	c = 30.397(4) Å	γ = 90°.
Volume	8399.6(18) $Å^3$	
Z	4	
Density (calculated)	0.957 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	2624	
Crystal size	0.58 x 0.21 x 0.21 mm^3	
Theta range for data collection	1.03 to 20.83°.	
Index ranges	-10<=h<=10, -25<=k<=25, -30<=l<=30	
Reflections collected	58181	
Independent reflections	8795 [R(int) = 0.0560]	
Completeness to theta = 20.83°	99.9 %	
Absorption correction	Multi-sacn with SADABS	
Max. and min. transmission	0.9865 and 0.9634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8795 / 996 / 791	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0993, wR2 = 0.2633	
R indices (all data)	R1 = 0.1079, wR2 = 0.2706	
Absolute structure parameter	N/A	
Largest diff. peak and hole	0.417 and -0.383 $e.Å^{-3}$	

Table S13. Torsion angles [°] for **4**

C(5)-O(1)-C(4)-C(1)	53.8(8)	C(7)-C(8A)-C(9)-C(8)	-63.8(12)
C(5)-O(1)-C(4)-C(3)	-67.4(7)	C(7)-C(8)-C(9)-C(10)	-40.3(15)
C(5)-O(1)-C(4)-C(2)	172.9(8)	C(7)-C(8)-C(9)-C(8A)	63.6(12)
C(6)-N(1)-C(5)-O(2)	0.4(12)	N(1)-C(6)-C(10)-C(11)	87.9(9)
C(6)-N(1)-C(5)-O(1)	-173.4(7)	C(7)-C(6)-C(10)-C(11)	-147.3(7)
C(4)-O(1)-C(5)-O(2)	9.8(10)	N(1)-C(6)-C(10)-C(9)	-149.7(7)
C(4)-O(1)-C(5)-N(1)	-176.1(5)	C(7)-C(6)-C(10)-C(9)	-24.8(9)
C(5)-N(1)-C(6)-C(7)	148.7(8)	C(8A)-C(9)-C(10)-C(11)	122.2(19)
C(5)-N(1)-C(6)-C(10)	-89.3(10)	C(8)-C(9)-C(10)-C(11)	161.5(10)
N(1)-C(6)-C(7)-C(8A)	164.9(17)	C(8A)-C(9)-C(10)-C(6)	1(2)
C(10)-C(6)-C(7)-C(8A)	38.7(18)	C(8)-C(9)-C(10)-C(6)	40.1(11)
N(1)-C(6)-C(7)-C(8)	125.7(12)	C(12)-N(2)-C(11)-O(3)	-4.6(10)
C(10)-C(6)-C(7)-C(8)	-0.5(13)	C(12)-N(2)-C(11)-C(10)	178.7(6)
C(6)-C(7)-C(8)-C(9)	25.4(16)	C(6)-C(10)-C(11)-O(3)	66.8(9)
C(8A)-C(7)-C(8)-C(9)	-63.6(12)	C(9)-C(10)-C(11)-O(3)	-50.3(10)
C(6)-C(7)-C(8A)-C(9)	-37(3)	C(6)-C(10)-C(11)-N(2)	-116.4(7)
C(8)-C(7)-C(8A)-C(9)	63.7(12)	C(9)-C(10)-C(11)-N(2)	126.5(7)
C(7)-C(8A)-C(9)-C(10)	23(3)	C(11)-N(2)-C(12)-C(16)	-84.9(8)

C(11)-N(2)-C(12)-C(13)	161.6(6)	N(4)-C(26)-C(27)-C(28)	166.3(7)
N(2)-C(12)-C(13)-C(14)	156.7(7)	C(30)-C(26)-C(27)-C(28)	45.9(9)
C(16)-C(12)-C(13)-C(14)	36.7(8)	C(26)-C(27)-C(28)-C(32)	72.8(10)
C(12)-C(13)-C(14)-C(17)	-165.6(8)	C(26)-C(27)-C(28)-C(31)	-159.2(8)
C(12)-C(13)-C(14)-C(15)	-43.5(9)	C(26)-C(27)-C(28)-C(29)	-44.4(8)
C(12)-C(13)-C(14)-C(18)	74.8(9)	C(32)-C(28)-C(29)-C(30)	-92.5(10)
C(17)-C(14)-C(15)-C(16)	154.2(8)	C(31)-C(28)-C(29)-C(30)	148.4(9)
C(13)-C(14)-C(15)-C(16)	30.6(8)	C(27)-C(28)-C(29)-C(30)	28.3(9)
C(18)-C(14)-C(15)-C(16)	-90.1(9)	C(28)-C(29)-C(30)-C(26)	-0.9(9)
N(2)-C(12)-C(16)-C(19)	100.0(7)	C(28)-C(29)-C(30)-C(33)	117.6(8)
C(13)-C(12)-C(16)-C(19)	-141.7(7)	N(4)-C(26)-C(30)-C(29)	-144.4(8)
N(2)-C(12)-C(16)-C(15)	-136.0(6)	C(27)-C(26)-C(30)-C(29)	-27.4(9)
C(13)-C(12)-C(16)-C(15)	-17.8(8)	N(4)-C(26)-C(30)-C(33)	95.0(9)
C(14)-C(15)-C(16)-C(19)	117.5(8)	C(27)-C(26)-C(30)-C(33)	-148.0(7)
C(14)-C(15)-C(16)-C(12)	-7.3(8)	C(34)-N(5)-C(33)-O(6)	-0.3(12)
C(20)-N(3)-C(19)-O(4)	1.7(13)	C(34)-N(5)-C(33)-C(30)	-179.7(7)
C(20)-N(3)-C(19)-C(16)	-176.7(8)	C(29)-C(30)-C(33)-O(6)	-37.3(10)
C(12)-C(16)-C(19)-O(4)	66.2(10)	C(26)-C(30)-C(33)-O(6)	79.6(10)
C(15)-C(16)-C(19)-O(4)	-53.7(10)	C(29)-C(30)-C(33)-N(5)	142.1(8)
C(12)-C(16)-C(19)-N(3)	-115.4(8)	C(26)-C(30)-C(33)-N(5)	-101.0(8)
C(15)-C(16)-C(19)-N(3)	124.7(8)	C(33)-N(5)-C(34)-C(38)	-99.1(9)
C(19)-N(3)-C(20)-C(24)	-99.1(9)	C(33)-N(5)-C(34)-C(35)	146.7(8)
C(19)-N(3)-C(20)-C(21)	141.0(8)	N(5)-C(34)-C(35)-C(36A)	176(5)
N(3)-C(20)-C(21)-C(22)	117.6(9)	C(38)-C(34)-C(35)-C(36A)	55(5)
C(24)-C(20)-C(21)-C(22)	-4.3(10)	N(5)-C(34)-C(35)-C(36)	158.9(11)
N(3)-C(20)-C(21)-C(22A)	168.5(12)	C(38)-C(34)-C(35)-C(36)	37.7(11)
C(24)-C(20)-C(21)-C(22A)	46.5(12)	C(34)-C(35)-C(36)-C(37)	-26.1(17)
C(22A)-C(21)-C(22)-C(23)	-47.8(14)	C(36A)-C(35)-C(36)-C(37)	-74(6)
C(20)-C(21)-C(22)-C(23)	36.6(13)	C(34)-C(35)-C(36A)-C(37)	-59(12)
C(22)-C(21)-C(22A)-C(23)	47.8(14)	C(36)-C(35)-C(36A)-C(37)	74(6)
C(20)-C(21)-C(22A)-C(23)	-53(2)	C(35)-C(36)-C(37)-C(36A)	75(6)
C(21)-C(22A)-C(23)-C(22)	-47.8(14)	C(35)-C(36)-C(37)-C(38)	4.2(18)
C(21)-C(22A)-C(23)-C(24)	40(2)	C(35)-C(36A)-C(37)-C(36)	-75(6)
C(21)-C(22)-C(23)-C(22A)	47.9(14)	C(35)-C(36A)-C(37)-C(38)	41(13)
C(21)-C(22)-C(23)-C(24)	-50.5(12)	C(36)-C(37)-C(38)-C(39)	138.4(13)
N(3)-C(20)-C(24)-C(25)	95.5(9)	C(36A)-C(37)-C(38)-C(39)	116(7)
C(21)-C(20)-C(24)-C(25)	-142.9(7)	C(36)-C(37)-C(38)-C(34)	19.2(14)
N(3)-C(20)-C(24)-C(23)	-147.0(7)	C(36A)-C(37)-C(38)-C(34)	-4(7)
C(21)-C(20)-C(24)-C(23)	-25.4(8)	N(5)-C(34)-C(38)-C(39)	88.2(8)
C(22A)-C(23)-C(24)-C(25)	115.3(14)	C(35)-C(34)-C(38)-C(39)	-152.4(7)
C(22)-C(23)-C(24)-C(25)	166.8(9)	N(5)-C(34)-C(38)-C(37)	-153.7(7)
C(22A)-C(23)-C(24)-C(20)	-7.2(14)	C(35)-C(34)-C(38)-C(37)	-34.3(8)
C(22)-C(23)-C(24)-C(20)	44.2(9)	C(40)-N(6)-C(39)-O(7)	0.9(12)
C(26)-N(4)-C(25)-O(5)	1.6(12)	C(40)-N(6)-C(39)-C(38)	-178.2(7)
C(26)-N(4)-C(25)-C(24)	176.2(7)	C(37)-C(38)-C(39)-O(7)	-37.8(11)
C(20)-C(24)-C(25)-O(5)	73.4(11)	C(34)-C(38)-C(39)-O(7)	76.9(9)
C(23)-C(24)-C(25)-O(5)	-41.4(12)	C(37)-C(38)-C(39)-N(6)	141.2(8)
C(20)-C(24)-C(25)-N(4)	-100.9(9)	C(34)-C(38)-C(39)-N(6)	-104.1(8)
C(23)-C(24)-C(25)-N(4)	144.3(7)	C(39)-N(6)-C(40)-C(44)	-103.0(8)
C(25)-N(4)-C(26)-C(30)	-105.6(9)	C(39)-N(6)-C(40)-C(41)	142.1(7)
C(25)-N(4)-C(26)-C(27)	140.4(8)	N(6)-C(40)-C(41)-C(42)	162.4(7)

C(44)-C(40)-C(41)-C(42)	41.4(8)	N(8)-C(54)-C(55)-C(56)	104.7(8)
C(40)-C(41)-C(42)-C(46)	75.9(9)	C(58)-C(54)-C(55)-C(56)	-17.0(8)
C(40)-C(41)-C(42)-C(45)	-160.3(8)	C(54)-C(55)-C(56)-C(60)	156.8(8)
C(40)-C(41)-C(42)-C(43)	-39.9(8)	C(54)-C(55)-C(56)-C(57)	32.1(8)
C(46)-C(42)-C(43)-C(44)	-94.6(8)	C(54)-C(55)-C(56)-C(59)	-80.5(8)
C(45)-C(42)-C(43)-C(44)	141.7(8)	C(60)-C(56)-C(57)-C(58)	-160.3(8)
C(41)-C(42)-C(43)-C(44)	24.8(9)	C(55)-C(56)-C(57)-C(58)	-35.9(8)
N(6)-C(40)-C(44)-C(43)	-142.1(7)	C(59)-C(56)-C(57)-C(58)	79.1(8)
C(41)-C(40)-C(44)-C(43)	-25.2(8)	C(56)-C(57)-C(58)-C(54)	26.6(9)
N(6)-C(40)-C(44)-C(47)	98.8(8)	C(56)-C(57)-C(58)-C(61)	150.2(7)
C(41)-C(40)-C(44)-C(47)	-144.3(6)	N(8)-C(54)-C(58)-C(57)	-125.9(7)
C(42)-C(43)-C(44)-C(40)	-0.5(9)	C(55)-C(54)-C(58)-C(57)	-6.2(8)
C(42)-C(43)-C(44)-C(47)	117.8(8)	N(8)-C(54)-C(58)-C(61)	114.6(8)
C(48)-N(7)-C(47)-O(8)	5.2(11)	C(55)-C(54)-C(58)-C(61)	-125.7(8)
C(48)-N(7)-C(47)-C(44)	176.5(6)	C(57)-C(58)-C(61)-O(11)	67.9(12)
C(40)-C(44)-C(47)-O(8)	71.1(9)	C(54)-C(58)-C(61)-O(11)	-172.3(10)
C(43)-C(44)-C(47)-O(8)	-44.9(10)	C(57)-C(58)-C(61)-O(10)	-103.3(10)
C(40)-C(44)-C(47)-N(7)	-100.4(8)	C(54)-C(58)-C(61)-O(10)	16.5(13)
C(43)-C(44)-C(47)-N(7)	143.7(7)	C(57)-C(58)-C(61)-O(11A)	83(2)
C(47)-N(7)-C(48)-C(49)	132.0(7)	C(54)-C(58)-C(61)-O(11A)	-157(2)
C(47)-N(7)-C(48)-C(52)	-112.9(7)	O(10)-C(61)-O(11)-C(62)	-2.2(19)
N(7)-C(48)-C(49)-C(50)	154.5(5)	O(11A)-C(61)-O(11)-C(62)	126(10)
C(52)-C(48)-C(49)-C(50)	36.1(6)	C(58)-C(61)-O(11)-C(62)	-173.4(10)
N(7)-C(48)-C(49)-C(50A)	106.4(6)	C(61)-O(11)-C(62)-C(63)	86.4(17)
C(52)-C(48)-C(49)-C(50A)	-12.0(6)	O(11)-C(62)-C(63)-C(64)	95.2(14)
C(48)-C(49)-C(50)-C(51)	-45.4(6)	O(11)-C(62)-C(63)-C(68)	-84.5(14)
C(50A)-C(49)-C(50)-C(51)	56.2(6)	C(68)-C(63)-C(64)-C(65)	0.0
C(50)-C(49)-C(50A)-C(51)	-56.6(6)	C(62)-C(63)-C(64)-C(65)	-179.7(10)
C(48)-C(49)-C(50A)-C(51)	33.1(6)	C(63)-C(64)-C(65)-C(66)	0.0
C(49)-C(50A)-C(51)-C(52)	-42.6(6)	C(64)-C(65)-C(66)-C(67)	0.0
C(49)-C(50A)-C(51)-C(50)	55.8(6)	C(65)-C(66)-C(67)-C(68)	0.0
C(49)-C(50)-C(51)-C(52)	38.3(6)	C(66)-C(67)-C(68)-C(63)	0.0
C(49)-C(50)-C(51)-C(50A)	-57.4(7)	C(64)-C(63)-C(68)-C(67)	0.0
C(50A)-C(51)-C(52)-C(53)	157.9(5)	C(62)-C(63)-C(68)-C(67)	179.6(11)
C(50)-C(51)-C(52)-C(53)	108.3(6)	O(11)-C(61)-O(11A)-C(62A)	-49(8)
C(50A)-C(51)-C(52)-C(48)	34.9(6)	O(10)-C(61)-O(11A)-C(62A)	14(4)
C(50)-C(51)-C(52)-C(48)	-14.7(6)	C(58)-C(61)-O(11A)-C(62A)	-173(2)
N(7)-C(48)-C(52)-C(51)	-130.4(6)	C(61)-O(11A)-C(62A)-C(63A)	73(4)
C(49)-C(48)-C(52)-C(51)	-13.7(7)	O(11A)-C(62A)-C(63A)-C(64A)	76(3)
N(7)-C(48)-C(52)-C(53)	105.7(7)	O(11A)-C(62A)-C(63A)-C(68A)	-104(3)
C(49)-C(48)-C(52)-C(53)	-137.7(7)	C(68A)-C(63A)-C(64A)-C(65A)	0.0
C(54)-N(8)-C(53)-O(9)	5.4(11)	C(62A)-C(63A)-C(64A)-C(65A)	-179.8(8)
C(54)-N(8)-C(53)-C(52)	-178.9(6)	C(63A)-C(64A)-C(65A)-C(66A)	0.0
C(51)-C(52)-C(53)-O(9)	-28.0(10)	C(64A)-C(65A)-C(66A)-C(67A)	0.0
C(48)-C(52)-C(53)-O(9)	90.3(8)	C(65A)-C(66A)-C(67A)-C(68A)	0.0
C(51)-C(52)-C(53)-N(8)	156.0(6)	C(66A)-C(67A)-C(68A)-C(63A)	0.0
C(48)-C(52)-C(53)-N(8)	-85.6(8)	C(64A)-C(63A)-C(68A)-C(67A)	0.0
C(53)-N(8)-C(54)-C(58)	-71.5(9)	C(62A)-C(63A)-C(68A)-C(67A)	179.8(8)
C(53)-N(8)-C(54)-C(55)	172.4(7)		

Symmetry transformations used to generate equivalent atoms:

Table S14. Hydrogen bonds for **4** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(8)#1	0.88	2.04	2.877(8)	158.9
N(2)-H(2)...O(9)#2	0.88	2.01	2.878(8)	166.8
N(3)-H(3)...O(2)	0.88	2.06	2.884(8)	156.2
N(4)-H(4)...O(3)	0.88	2.04	2.843(9)	152.0
N(5)-H(5)...O(4)	0.88	1.99	2.843(8)	162.6
N(6)-H(6)...O(5)	0.88	1.96	2.792(9)	157.0
N(7)-H(7)...O(6)	0.88	2.05	2.866(7)	154.4
N(8)-H(8)...O(7)	0.88	2.05	2.896(8)	161.4

Symmetry transformations used to generate equivalent atoms:
#1 -x-1/2,-y+1,z+1/2 #2 -x+1/2,-y+1,z+1/2

Boc-ACPC-ACPC-ACPC-β^3-hPhe-ACPC-ACPC-Aib-OPBB (5)

*The two data sets for heptamer **5** were obtained for crystals grown under different conditions. The refinement of the structural data for crystals grown from water-methanol solution is incomplete due to low resolution. The report for crystals grown from isopropanol solution is given below.*

Data Collection

A colorless crystal with approximate dimensions 0.39 x 0.28 x 0.14 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100.0(3) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu K_α (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 50 frames collected at intervals of 0.5º in a 25º range about ω with the exposure time of 5 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the SMART program. The final cell constants were calculated from a set of 9245 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.82 Å. A total of 47947 data were harvested by collecting 18 sets of frames with 0.6º scans in ω with an exposure time 25-45 sec per frame depending on the 2θ value. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data and the E-statistics were uniquely consistent for the space group *P1* that yielded chemically reasonable and computationally stable results of refinement [S4].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares

cycles and difference Fourier maps. All non-hydrogen (except Br1a, Br2a, C13a-C15a and C13c-C15c) atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There are two symmetry independent foldamers and four molecules of ^{i}PrOH in the unit cell. They were refined as follows.

Foldmer Br1. It appears that there is a second position for the Br atom with an occupancy of 7.0(7)%. This was enough to refine this Br atom (Br1A) but not enough to identify the second position of the entire foldamer. Atom C14 is disordered over two positions in a 0.686(11):0.314(11) ratio. Atoms C19-C21 are disordered over two positions in a 0.649(12):0.351(12) ratio. Atoms C35-C37 are disordered over two positions in a 0.837(10):0.163(10) ratio.

Foldamer Br2. It appears that there is a second position for the Br atom with an occupancy of 6.3(5)%. This was enough to refine this Br atom (Br2A) but not enough to identify the second position of the entire foldamer. Atoms C13a-C15a are disordered over two positions in a 0.730(11):0.270(11) ratio and were refined with isotropic displacement coefficients. Atoms C25a-C31a are disordered over two positions in a 0.679(5):0.321(5) ratio.

Soft restraints were applied to all disordered parts.

Solvents. All ^{i}PrOH were refined with a geometry constrained to the idealized minimum energy conformation as optimized at the pbe1pbe/6-311++g(3df,3pd) level of theory.

The final least-squares refinement of 1255 parameters against 18942 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0689 and 0.1940, respectively. The final difference Fourier map was featureless.

References

[S1] Bruker-AXS. (2000-2007) SADABS, SAINT, SHELXTL, and SMART 5.622 Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.
[S1] Bruker-AXS. (2000-2003) SADABS V.2.05, SAINT V.6.22, SHELXTL V.6.10 & SMART 5.622 Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.
[S3] A.L. Spek (1990) Acta Cryst. A46, C34.
[S4] Sheldrick, G. M. (2008) SHELXL. Acta Cryst. A64, 112-122.

Table S15. Crystal data and structure refinement for heptamer **5**

Empirical formula	C_{62} H_{94} Br N_7 O_{12}	
Formula weight	1209.35	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 9.45820(10) Å	α= 105.2770(10)°.
	b = 15.6589(3) Å	β= 97.8850(10)°.
	c = 23.4440(4) Å	γ = 94.0840(10)°.
Volume	3296.80(9) $Å^3$	
Z	2	
Density (calculated)	1.218 Mg/m^3	
Absorption coefficient	1.352 mm^{-1}	
F(000)	1292	
Crystal size	0.39 x 0.28 x 0.14 mm^3	
Theta range for data collection	1.98 to 69.57°.	
Index ranges	-11<=h<=11, -15<=k<=18, -28<=l<=28	
Reflections collected	47947	
Independent reflections	18942 [R(int) = 0.0205]	
Completeness to theta = 69.57°	95.2 %	
Absorption correction	Empirical with SADABS	
Max. and min. transmission	0.8332 and 0.6206	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18942 / 59 / 1255	
Goodness-of-fit on F^2	0.987	
Final R indices [I>2sigma(I)]	R1 = 0.0689, wR2 = 0.1916	
R indices (all data)	R1 = 0.0704, wR2 = 0.1940	
Absolute structure parameter	0.017(14)	
Largest diff. peak and hole	1.582 and -1.172 e.$Å^{-3}$	

Table S16. Torsion angles [°] for **5**

C(5)-O(1)-C(4)-C(1)	-54.1(6)	C(7)-C(6)-C(10)-C(11)	-161.9(4)
C(5)-O(1)-C(4)-C(2)	71.4(6)	N(1)-C(6)-C(10)-C(9)	-162.3(4)
C(5)-O(1)-C(4)-C(3)	-172.3(4)	C(7)-C(6)-C(10)-C(9)	-38.8(4)
C(4)-O(1)-C(5)-O(2)	-6.2(6)	C(12)-N(2)-C(11)-O(3)	-6.2(6)
C(4)-O(1)-C(5)-N(1)	173.9(4)	C(12)-N(2)-C(11)-C(10)	173.5(4)
C(6)-N(1)-C(5)-O(2)	-2.6(7)	C(9)-C(10)-C(11)-O(3)	-50.7(5)
C(6)-N(1)-C(5)-O(1)	177.3(4)	C(6)-C(10)-C(11)-O(3)	65.9(5)
C(5)-N(1)-C(6)-C(7)	138.2(4)	C(9)-C(10)-C(11)-N(2)	129.6(4)
C(5)-N(1)-C(6)-C(10)	-105.0(5)	C(6)-C(10)-C(11)-N(2)	-113.7(4)
N(1)-C(6)-C(7)-C(8)	166.8(4)	C(11)-N(2)-C(12)-C(13)	166.8(4)
C(10)-C(6)-C(7)-C(8)	42.9(4)	C(11)-N(2)-C(12)-C(16)	-76.2(5)
C(6)-C(7)-C(8)-C(9)	-30.2(5)	N(2)-C(12)-C(13)-C(14B)	159.3(8)
C(7)-C(8)-C(9)-C(10)	5.7(5)	C(16)-C(12)-C(13)-C(14B)	38.4(9)
C(8)-C(9)-C(10)-C(11)	141.1(4)	N(2)-C(12)-C(13)-C(14)	104.0(5)
C(8)-C(9)-C(10)-C(6)	20.5(5)	C(16)-C(12)-C(13)-C(14)	-16.9(6)
N(1)-C(6)-C(10)-C(11)	74.5(5)	C(14B)-C(13)-C(14)-C(15)	-53.8(8)

C(12)-C(13)-C(14)-C(15)	38.4(4)	C(18)-C(22)-C(23)-O(5)	77.4(5)
C(16)-C(15)-C(14)-C(13)	-45.0(3)	C(21)-C(22)-C(23)-O(5)	-48.0(7)
C(14B)-C(15)-C(14)-C(13)	51.7(8)	C(21B)-C(22)-C(23)-O(5)	-29.8(10)
C(14)-C(13)-C(14B)-C(15)	52.6(7)	C(18)-C(22)-C(23)-N(4)	-100.3(4)
C(12)-C(13)-C(14B)-C(15)	-49.3(11)	C(21)-C(22)-C(23)-N(4)	134.3(6)
C(16)-C(15)-C(14B)-C(13)	42.3(12)	C(21B)-C(22)-C(23)-N(4)	152.5(9)
C(14)-C(15)-C(14B)-C(13)	-52.3(8)	C(23)-N(4)-C(24)-C(25)	145.9(4)
C(14)-C(15)-C(16)-C(17)	156.7(3)	C(23)-N(4)-C(24)-C(32)	-93.0(5)
C(14B)-C(15)-C(16)-C(17)	105.2(8)	N(4)-C(24)-C(25)-C(26)	-68.7(5)
C(14)-C(15)-C(16)-C(12)	34.1(3)	C(32)-C(24)-C(25)-C(26)	169.8(4)
C(14B)-C(15)-C(16)-C(12)	-17.3(8)	C(24)-C(25)-C(26)-C(31)	-86.3(6)
N(2)-C(12)-C(16)-C(17)	104.1(4)	C(24)-C(25)-C(26)-C(27)	94.0(6)
C(13)-C(12)-C(16)-C(17)	-134.5(4)	C(31)-C(26)-C(27)-C(28)	0.4(8)
N(2)-C(12)-C(16)-C(15)	-133.1(4)	C(25)-C(26)-C(27)-C(28)	-179.8(5)
C(13)-C(12)-C(16)-C(15)	-11.7(5)	C(26)-C(27)-C(28)-C(29)	-1.3(9)
C(18)-N(3)-C(17)-O(4)	-2.3(7)	C(27)-C(28)-C(29)-C(30)	1.7(10)
C(18)-N(3)-C(17)-C(16)	-179.6(4)	C(28)-C(29)-C(30)-C(31)	-1.4(11)
C(15)-C(16)-C(17)-O(4)	-55.2(6)	C(29)-C(30)-C(31)-C(26)	0.5(10)
C(12)-C(16)-C(17)-O(4)	63.2(5)	C(27)-C(26)-C(31)-C(30)	-0.1(8)
C(15)-C(16)-C(17)-N(3)	122.2(4)	C(25)-C(26)-C(31)-C(30)	-179.8(5)
C(12)-C(16)-C(17)-N(3)	-119.3(4)	N(4)-C(24)-C(32)-C(33)	86.6(4)
C(17)-N(3)-C(18)-C(19B)	121.3(9)	C(25)-C(24)-C(32)-C(33)	-152.1(4)
C(17)-N(3)-C(18)-C(22)	-107.4(5)	C(34)-N(5)-C(33)-O(6)	-0.2(6)
C(17)-N(3)-C(18)-C(19)	142.2(6)	C(34)-N(5)-C(33)-C(32)	179.3(4)
N(3)-C(18)-C(22)-C(23)	95.7(4)	C(24)-C(32)-C(33)-O(6)	68.3(5)
C(19B)-C(18)-C(22)-C(23)	-141.4(9)	C(24)-C(32)-C(33)-N(5)	-111.2(4)
C(19)-C(18)-C(22)-C(23)	-144.2(5)	C(33)-N(5)-C(34)-C(35B)	132(2)
N(3)-C(18)-C(22)-C(21)	-140.0(5)	C(33)-N(5)-C(34)-C(35)	137.5(6)
C(19B)-C(18)-C(22)-C(21)	-17.0(11)	C(33)-N(5)-C(34)-C(38)	-106.0(4)
C(19)-C(18)-C(22)-C(21)	-19.9(6)	N(5)-C(34)-C(38)-C(39)	108.3(4)
N(3)-C(18)-C(22)-C(21B)	-140.9(8)	C(35B)-C(34)-C(38)-C(39)	-136(2)
C(19B)-C(18)-C(22)-C(21B)	-18.0(11)	C(35)-C(34)-C(38)-C(39)	-130.1(5)
C(19)-C(18)-C(22)-C(21B)	-20.8(9)	N(5)-C(34)-C(38)-C(37)	-125.9(5)
N(3)-C(18)-C(19)-C(20)	110.7(7)	C(35B)-C(34)-C(38)-C(37)	-10(2)
C(19B)-C(18)-C(19)-C(20)	179(3)	C(35)-C(34)-C(38)-C(37)	-4.2(6)
C(22)-C(18)-C(19)-C(20)	-7.5(7)	N(5)-C(34)-C(38)-C(37B)	-134.4(8)
C(18)-C(19)-C(20)-C(21)	31.6(9)	C(35B)-C(34)-C(38)-C(37B)	-19(2)
C(19)-C(20)-C(21)-C(22)	-40.6(8)	C(35)-C(34)-C(38)-C(37B)	-12.8(9)
C(23)-C(22)-C(21)-C(20)	164.6(5)	N(5)-C(34)-C(35)-C(36)	100.7(6)
C(18)-C(22)-C(21)-C(20)	38.8(7)	C(35B)-C(34)-C(35)-C(36)	128(14)
C(21B)-C(22)-C(21)-C(20)	42(3)	C(38)-C(34)-C(35)-C(36)	-20.7(7)
N(3)-C(18)-C(19B)-C(20B)	119.0(10)	C(34)-C(35)-C(36)-C(37)	38.0(7)
C(22)-C(18)-C(19B)-C(20B)	-7.2(14)	C(39)-C(38)-C(37)-C(36)	148.7(5)
C(19)-C(18)-C(19B)-C(20B)	0.5(18)	C(34)-C(38)-C(37)-C(36)	26.4(7)
C(18)-C(19B)-C(20B)-C(21B)	30.2(15)	C(37B)-C(38)-C(37)-C(36)	69(4)
C(19B)-C(20B)-C(21B)-C(22)	-44.5(16)	C(35)-C(36)-C(37)-C(38)	-39.9(7)
C(23)-C(22)-C(21B)-C(20B)	152.7(10)	N(5)-C(34)-C(35B)-C(36B)	159(2)
C(18)-C(22)-C(21B)-C(20B)	34.8(12)	C(35)-C(34)-C(35B)-C(36B)	5(11)
C(21)-C(22)-C(21B)-C(20B)	-143(4)	C(38)-C(34)-C(35B)-C(36B)	38(3)
C(24)-N(4)-C(23)-O(5)	-2.9(7)	C(34)-C(35B)-C(36B)-C(37B)	-42(3)
C(24)-N(4)-C(23)-C(22)	174.8(4)	C(35B)-C(36B)-C(37B)-C(38)	34(3)

C(39)-C(38)-C(37B)-C(36B)	106.0(15)	C(53)-C(54)-C(55)-C(56)	3.3(7)
C(37)-C(38)-C(37B)-C(36B)	-148(5)	Br(1A)-C(54)-C(55)-C(56)	-173.4(6)
C(34)-C(38)-C(37B)-C(36B)	-9.0(16)	Br(1)-C(54)-C(55)-C(56)	-177.7(4)
C(40)-N(6)-C(39)-O(7)	-8.0(7)	C(53)-C(54)-C(55)-Br(1A)	176.7(8)
C(40)-N(6)-C(39)-C(38)	168.9(4)	Br(1)-C(54)-C(55)-Br(1A)	-4.3(5)
C(37)-C(38)-C(39)-O(7)	-40.3(7)	C(54)-Br(1A)-C(55)-C(56)	17.0(16)
C(34)-C(38)-C(39)-O(7)	80.8(5)	C(54)-C(55)-C(56)-C(51)	-1.7(7)
C(37B)-C(38)-C(39)-O(7)	-26.9(11)	Br(1A)-C(55)-C(56)-C(51)	-14.4(17)
C(37)-C(38)-C(39)-N(6)	142.8(5)	C(52)-C(51)-C(56)-C(55)	-0.9(7)
C(34)-C(38)-C(39)-N(6)	-96.1(4)	C(50)-C(51)-C(56)-C(55)	179.3(4)
C(37B)-C(38)-C(39)-N(6)	156.2(10)	C(5A)-O(11)-C(4A)-C(1A)	-56.9(6)
C(39)-N(6)-C(40)-C(41)	135.3(4)	C(5A)-O(11)-C(4A)-C(3A)	-174.5(4)
C(39)-N(6)-C(40)-C(44)	-107.2(4)	C(5A)-O(11)-C(4A)-C(2A)	67.8(6)
N(6)-C(40)-C(41)-C(42)	160.0(3)	C(6A)-N(8)-C(5A)-O(12)	-1.1(7)
C(44)-C(40)-C(41)-C(42)	38.4(4)	C(6A)-N(8)-C(5A)-O(11)	178.8(4)
C(40)-C(41)-C(42)-C(43)	-43.6(4)	C(4A)-O(11)-C(5A)-O(12)	-6.0(6)
C(41)-C(42)-C(43)-C(44)	31.9(5)	C(4A)-O(11)-C(5A)-N(8)	174.1(4)
C(42)-C(43)-C(44)-C(45)	109.1(4)	C(5A)-N(8)-C(6A)-C(7A)	132.8(4)
C(42)-C(43)-C(44)-C(40)	-8.2(5)	C(5A)-N(8)-C(6A)-C(10A)	-110.4(5)
N(6)-C(40)-C(44)-C(45)	97.8(4)	N(8)-C(6A)-C(7A)-C(8A)	167.2(4)
C(41)-C(40)-C(44)-C(45)	-139.8(3)	C(10A)-C(6A)-C(7A)-C(8A)	43.9(4)
N(6)-C(40)-C(44)-C(43)	-141.3(4)	C(6A)-C(7A)-C(8A)-C(9A)	-31.1(5)
C(41)-C(40)-C(44)-C(43)	-18.9(4)	C(7A)-C(8A)-C(9A)-C(10A)	6.2(6)
C(46)-N(7)-C(45)-O(8)	-4.1(6)	C(8A)-C(9A)-C(10A)-C(11A)	140.5(4)
C(46)-N(7)-C(45)-C(44)	171.6(3)	C(8A)-C(9A)-C(10A)-C(6A)	20.6(5)
C(43)-C(44)-C(45)-O(8)	-25.1(5)	N(8)-C(6A)-C(10A)-C(11A)	74.7(5)
C(40)-C(44)-C(45)-O(8)	90.7(4)	C(7A)-C(6A)-C(10A)-C(11A)	-162.3(4)
C(43)-C(44)-C(45)-N(7)	159.2(3)	N(8)-C(6A)-C(10A)-C(9A)	-162.9(4)
C(40)-C(44)-C(45)-N(7)	-84.9(4)	C(7A)-C(6A)-C(10A)-C(9A)	-39.9(5)
C(45)-N(7)-C(46)-C(48)	167.6(3)	C(12A)-N(9)-C(11A)-O(13)	-5.8(7)
C(45)-N(7)-C(46)-C(47)	-70.5(5)	C(12A)-N(9)-C(11A)-C(10A)	171.5(4)
C(45)-N(7)-C(46)-C(49)	50.6(5)	C(9A)-C(10A)-C(11A)-O(13)	-48.2(6)
C(50)-O(10)-C(49)-O(9)	5.6(6)	C(6A)-C(10A)-C(11A)-O(13)	67.5(5)
C(50)-O(10)-C(49)-C(46)	-177.9(3)	C(9A)-C(10A)-C(11A)-N(9)	134.4(4)
N(7)-C(46)-C(49)-O(9)	-141.4(4)	C(6A)-C(10A)-C(11A)-N(9)	-109.8(4)
C(48)-C(46)-C(49)-O(9)	100.8(5)	C(11A)-N(9)-C(12A)-C(13C)	156.3(11)
C(47)-C(46)-C(49)-O(9)	-19.6(6)	C(11A)-N(9)-C(12A)-C(16A)	-75.4(6)
N(7)-C(46)-C(49)-O(10)	42.0(5)	C(11A)-N(9)-C(12A)-C(13A)	170.6(5)
C(48)-C(46)-C(49)-O(10)	-75.8(4)	N(9)-C(12A)-C(16A)-C(17A)	102.8(5)
C(47)-C(46)-C(49)-O(10)	163.8(4)	C(13C)-C(12A)-C(16A)-C(17A)	-132.3(13)
C(49)-O(10)-C(50)-C(51)	135.6(4)	C(13A)-C(12A)-C(16A)-C(17A)	-136.5(5)
O(10)-C(50)-C(51)-C(52)	3.0(6)	N(9)-C(12A)-C(16A)-C(15A)	-133.9(6)
O(10)-C(50)-C(51)-C(56)	-177.2(4)	C(13C)-C(12A)-C(16A)-C(15A)	-9.0(14)
C(56)-C(51)-C(52)-C(53)	2.0(7)	C(13A)-C(12A)-C(16A)-C(15A)	-13.2(8)
C(50)-C(51)-C(52)-C(53)	-178.2(4)	N(9)-C(12A)-C(16A)-C(15C)	-131.5(14)
C(51)-C(52)-C(53)-C(54)	-0.4(7)	C(13C)-C(12A)-C(16A)-C(15C)	-6.7(19)
C(52)-C(53)-C(54)-C(55)	-2.3(7)	C(13A)-C(12A)-C(16A)-C(15C)	-10.9(14)
C(52)-C(53)-C(54)-Br(1A)	173.0(8)	N(9)-C(12A)-C(13A)-C(14A)	104.9(8)
C(52)-C(53)-C(54)-Br(1)	178.7(3)	C(13C)-C(12A)-C(13A)-C(14A)	-179(6)
C(55)-Br(1A)-C(54)-C(53)	-175.9(10)	C(16A)-C(12A)-C(13A)-C(14A)	-14.9(9)
C(55)-Br(1A)-C(54)-Br(1)	167.0(14)	C(12A)-C(13A)-C(14A)-C(15A)	36.6(10)

C(17A)-C(16A)-C(15A)-C(14A)	157.2(6)	C(29A)-C(30A)-C(31A)-C(26A)	0.0
C(15C)-C(16A)-C(15A)-C(14A)	21(8)	C(27A)-C(26A)-C(31A)-C(30A)	0.0
C(12A)-C(16A)-C(15A)-C(14A)	32.8(8)	C(25A)-C(26A)-C(31A)-C(30A)	-178.0(6)
C(13A)-C(14A)-C(15A)-C(16A)	-42.1(9)	N(11)-C(24A)-C(25B)-C(26B)	-80(2)
N(9)-C(12A)-C(13C)-C(14C)	153.5(14)	C(32A)-C(24A)-C(25B)-C(26B)	156.1(15)
C(16A)-C(12A)-C(13C)-C(14C)	27(2)	C(25A)-C(24A)-C(25B)-C(26B)	-121(16)
C(13A)-C(12A)-C(13C)-C(14C)	45(4)	C(24A)-C(25B)-C(26B)-C(27B)	97.8(19)
C(12A)-C(13C)-C(14C)-C(15C)	-35(2)	C(24A)-C(25B)-C(26B)-C(31B)	-80(2)
C(17A)-C(16A)-C(15C)-C(14C)	105.6(16)	C(31B)-C(26B)-C(27B)-C(28B)	0.0
C(15A)-C(16A)-C(15C)-C(14C)	153(10)	C(25B)-C(26B)-C(27B)-C(28B)	-177.9(7)
C(12A)-C(16A)-C(15C)-C(14C)	-16(2)	C(26B)-C(27B)-C(28B)-C(29B)	0.0
C(13C)-C(14C)-C(15C)-C(16A)	35(3)	C(27B)-C(28B)-C(29B)-C(30B)	0.0
C(18A)-N(10)-C(17A)-O(14)	-2.6(7)	C(28B)-C(29B)-C(30B)-C(31B)	0.0
C(18A)-N(10)-C(17A)-C(16A)	179.9(4)	C(29B)-C(30B)-C(31B)-C(26B)	0.0
C(15A)-C(16A)-C(17A)-O(14)	-60.6(7)	C(27B)-C(26B)-C(31B)-C(30B)	0.0
C(15C)-C(16A)-C(17A)-O(14)	-51.9(11)	C(25B)-C(26B)-C(31B)-C(30B)	177.6(8)
C(12A)-C(16A)-C(17A)-O(14)	61.4(6)	N(11)-C(24A)-C(32A)-C(33A)	86.8(3)
C(15A)-C(16A)-C(17A)-N(10)	117.0(6)	C(25A)-C(24A)-C(32A)-C(33A)	-153.6(8)
C(15C)-C(16A)-C(17A)-N(10)	125.6(11)	C(25B)-C(24A)-C(32A)-C(33A)	-148.6(15)
C(12A)-C(16A)-C(17A)-N(10)	-121.0(4)	C(34A)-N(12)-C(33A)-O(16)	1.3(5)
C(17A)-N(10)-C(18A)-C(22A)	-104.4(5)	C(34A)-N(12)-C(33A)-C(32A)	-179.0(2)
C(17A)-N(10)-C(18A)-C(19A)	141.4(5)	C(24A)-C(32A)-C(33A)-O(16)	74.8(3)
N(10)-C(18A)-C(19A)-C(20A)	109.0(5)	C(24A)-C(32A)-C(33A)-N(12)	-104.9(3)
C(22A)-C(18A)-C(19A)-C(20A)	-10.9(6)	C(33A)-N(12)-C(34A)-C(35A)	130.5(3)
C(18A)-C(19A)-C(20A)-C(21A)	35.6(6)	C(33A)-N(12)-C(34A)-C(38A)	-111.3(3)
C(19A)-C(20A)-C(21A)-C(22A)	-45.9(6)	N(12)-C(34A)-C(35A)-C(36A)	157.87(17)
C(20A)-C(21A)-C(22A)-C(23A)	164.5(5)	C(38A)-C(34A)-C(35A)-C(36A)	35.1
C(20A)-C(21A)-C(22A)-C(18A)	39.8(6)	C(34A)-C(35A)-C(36A)-C(37A)	-45.4
N(10)-C(18A)-C(22A)-C(21A)	-138.9(4)	C(35A)-C(36A)-C(37A)-C(38A)	38.1
C(19A)-C(18A)-C(22A)-C(21A)	-18.1(5)	C(36A)-C(37A)-C(38A)-C(39A)	102.6
N(10)-C(18A)-C(22A)-C(23A)	96.5(5)	C(36A)-C(37A)-C(38A)-C(34A)	-16.4
C(19A)-C(18A)-C(22A)-C(23A)	-142.6(4)	N(12)-C(34A)-C(38A)-C(39A)	103.41(17)
C(24A)-N(11)-C(23A)-O(15)	-1.1(7)	C(35A)-C(34A)-C(38A)-C(39A)	-134.5
C(24A)-N(11)-C(23A)-C(22A)	177.8(4)	N(12)-C(34A)-C(38A)-C(37A)	-133.93(17)
C(21A)-C(22A)-C(23A)-O(15)	-45.8(6)	C(35A)-C(34A)-C(38A)-C(37A)	-11.8
C(18A)-C(22A)-C(23A)-O(15)	75.4(5)	C(40A)-N(13)-C(39A)-O(17)	-6.6(4)
C(21A)-C(22A)-C(23A)-N(11)	135.3(5)	C(40A)-N(13)-C(39A)-C(38A)	170.10(19)
C(18A)-C(22A)-C(23A)-N(11)	-103.5(5)	C(37A)-C(38A)-C(39A)-O(17)	-28.48(19)
C(23A)-N(11)-C(24A)-C(32A)	-97.1(5)	C(34A)-C(38A)-C(39A)-O(17)	88.65(19)
C(23A)-N(11)-C(24A)-C(25A)	142.9(6)	C(37A)-C(38A)-C(39A)-N(13)	154.75(16)
C(23A)-N(11)-C(24A)-C(25B)	139.6(8)	C(34A)-C(38A)-C(39A)-N(13)	-88.12(16)
N(11)-C(24A)-C(25A)-C(26A)	-62.7(12)	C(39A)-N(13)-C(40A)-C(41A)	134.1(2)
C(32A)-C(24A)-C(25A)-C(26A)	176.6(9)	C(39A)-N(13)-C(40A)-C(44A)	-109.6(3)
C(25B)-C(24A)-C(25A)-C(26A)	78(13)	N(13)-C(40A)-C(41A)-C(42A)	161.11(15)
C(24A)-C(25A)-C(26A)-C(27A)	92.8(12)	C(44A)-C(40A)-C(41A)-C(42A)	39.9
C(24A)-C(25A)-C(26A)-C(31A)	-89.3(12)	C(40A)-C(41A)-C(42A)-C(43A)	-44.2
C(31A)-C(26A)-C(27A)-C(28A)	0.0	C(41A)-C(42A)-C(43A)-C(44A)	31.2
C(25A)-C(26A)-C(27A)-C(28A)	177.9(6)	C(42A)-C(43A)-C(44A)-C(45A)	109.5
C(26A)-C(27A)-C(28A)-C(29A)	0.0	C(42A)-C(43A)-C(44A)-C(40A)	-6.9
C(27A)-C(28A)-C(29A)-C(30A)	0.0	N(13)-C(40A)-C(44A)-C(45A)	97.45(15)
C(28A)-C(29A)-C(30A)-C(31A)	0.0	C(41A)-C(40A)-C(44A)-C(45A)	-140.7

N(13)-C(40A)-C(44A)-C(43A)	-142.45(15)	C(48A)-C(46A)-C(49A)-O(20)	-73.05(14)
C(41A)-C(40A)-C(44A)-C(43A)	-20.6	C(47A)-C(46A)-C(49A)-O(20)	166.36(14)
C(46A)-N(14)-C(45A)-O(18)	-4.0(4)	C(49A)-O(20)-C(50A)-C(51A)	131.60(19)
C(46A)-N(14)-C(45A)-C(44A)	171.87(17)	O(20)-C(50A)-C(51A)-C(52A)	5.68(12)
C(43A)-C(44A)-C(45A)-O(18)	-25.80(17)	O(20)-C(50A)-C(51A)-C(56A)	-175.63(13)
C(40A)-C(44A)-C(45A)-O(18)	89.73(17)	C(56A)-C(51A)-C(52A)-C(53A)	0.2
C(43A)-C(44A)-C(45A)-N(14)	158.34(16)	C(50A)-C(51A)-C(52A)-C(53A)	178.9
C(40A)-C(44A)-C(45A)-N(14)	-86.13(16)	C(51A)-C(52A)-C(53A)-C(54A)	2.2
C(45A)-N(14)-C(46A)-C(49A)	48.9(3)	C(52A)-C(53A)-C(54A)-C(55A)	-3.5
C(45A)-N(14)-C(46A)-C(48A)	168.1(2)	C(52A)-C(53A)-C(54A)-Br(2)	178.33(7)
C(45A)-N(14)-C(46A)-C(47A)	-71.6(3)	C(52A)-C(53A)-C(54A)-Br(2A)	-178.8(2)
C(50A)-O(20)-C(49A)-O(19)	7.2(4)	C(53A)-C(54A)-C(55A)-C(56A)	2.3
C(50A)-O(20)-C(49A)-C(46A)	-177.27(16)	Br(2)-C(54A)-C(55A)-C(56A)	-179.56(7)
N(14)-C(46A)-C(49A)-O(19)	-139.0(3)	Br(2A)-C(54A)-C(55A)-C(56A)	176.0(3)
C(48A)-C(46A)-C(49A)-O(19)	102.4(2)	C(54A)-C(55A)-C(56A)-C(51A)	0.3
C(47A)-C(46A)-C(49A)-O(19)	-18.2(2)	C(52A)-C(51A)-C(56A)-C(55A)	-1.5
N(14)-C(46A)-C(49A)-O(20)	45.47(19)	C(50A)-C(51A)-C(56A)-C(55A)	179.8

Symmetry transformations used to generate equivalent atoms:

Table S17. Hydrogen bonds for **5** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(8)#1	0.88	2.05	2.788(5)	141.2
N(2)-H(2N)...O(9)#1	0.88	2.10	2.960(5)	166.9
N(3)-H(3N)...O(2)	0.88	2.05	2.865(5)	153.5
N(4)-H(4N)...O(3)	0.88	2.04	2.807(5)	144.7
N(5)-H(5N)...O(4)	0.88	1.96	2.793(5)	156.4
N(6)-H(6N)...O(5)	0.88	2.03	2.855(4)	154.9
N(7)-H(7N)...O(6)	0.88	1.98	2.822(5)	160.5
N(8)-H(8N)...O(18)#1	0.88	2.03	2.805(5)	146.4
N(9)-H(9N)...O(19)#1	0.88	2.11	2.975(5)	165.9
N(10)-H(10N)...O(12)	0.88	2.08	2.902(5)	154.7
N(11)-H(11N)...O(13)	0.88	2.05	2.811(5)	144.8
N(12)-H(12N)...O(14)	0.88	1.96	2.794(5)	156.6
N(13)-H(13N)...O(15)	0.88	2.01	2.861(5)	162.3
N(14)-H(14N)...O(16)	0.88	2.01	2.854(5)	161.7
O(1S)-H(8S1)...O(6)	0.96	1.83	2.783(3)	172.4
O(2S)-H(8S2)...O(7)	0.96	1.93	2.814(3)	152.1

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z