Electronic Supplementary Information

Peptide-based capsules with chirality-controlled functionalized interiors – rational design and amplification from dynamic combinatorial libraries

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General information

All solvents and chemicals used were purchased from Sigma Aldrich, TCI Europe N. V., Roth, Chem Impex Inc. and Euriso-top, were of reagent grade and were used without further purification. High resolution ESI mass spectra were recorded on a SYNAPT spectrometer. ECD spectra were recorded on Jasco J-715 spectropolarimeter. Specific rotations were measured on Jasco P-2000 polarimeter. $[\alpha]_D^{22}$ are given in $degcm^3g^{-1}dm^{-1}$.

^1H and ^{13}C NMR spectra were recorded at 298 K on Bruker 400 MHz, Varian 500 MHz and Varian 600 MHz instruments with residual solvent signal as internal standard. All 2D NMR spectra were recorded at 298 K on Varian 600 MHz with residual solvent signal as internal standard. *J* values are given in Hz.

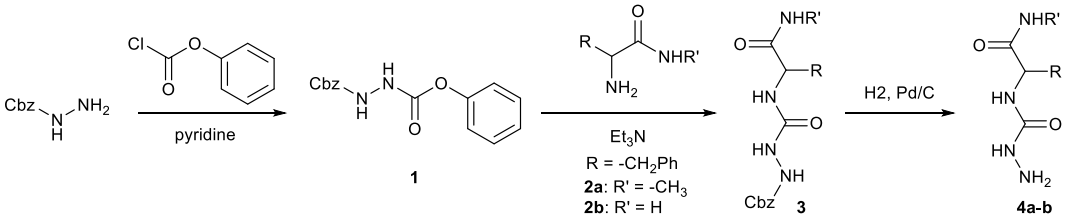
NMR DOSY experiments were performed on a Varian VNMRS-600 spectrometer equipped with a 5-mm PFG AutoXID ($^1H/X^{15}N$-^{31}P) probe at temperature 298 K. The samples for measurements were prepared by dissolution of *ca*. 10-20 mg of each substance in 0.6 ml of appropriate solvent ($CDCl_3$ or DMSO-D6). The gradient strength was calibrated using 1% H_2O in 99% D_2O sample and corrected for gradient non-uniformity using procedure implemented in Varian software.[1]

DOSY experiments were run with the ONESHOT or DPFGDSTE (with convection compensation) pulse sequences for measurements in DMSO-D6 and $CDCl_3$ solutions, respectively. The gradient strengths were incremented as a square dependence in the range from 6 to 55 G/cm. 64 transients were recorded for each increment with 2.5 s acquisition time and 1 s relaxation delay (overall experiment time of 60 min). Duration of magnetic field gradients (δ) was 2 ms, whereas diffusion delay (Δ) was chosen as 80-100 ms in $CDCl_3$ and 220-250 ms in DMSO-D6, respectively. Other parameters include the following: a sweep width of 12 000 Hz, 32K data points. The data were processed using Varian DOSY software.[2]

Synthetic procedures for peptides

Synthesis of AzaGly-PheNHMe 4a and AzaGly-PheNH$_2$ 4b[3]

N^{α}-CBz-hydrazide (2.493 g, 15 mmol) and pyridine (2.73 mL, 2.2 equiv) were dissolved, with stirring, in DCM (10 mL) and phenyl chloroformate (2.45 g, 1.1 equiv) in DCM (10 mL) was added dropwise over 30 min at 0 °C. The mixture was stirred overnight at room temperature, and DCM was evaporated under reduced pressure. The residue was dissolved in EtOAc (350 mL) and washed with 10% aqueous citric acid (50 mL), water (100 mL), 10% aqueous K_2CO_3 (50 mL), and water (50 mL). The organic phase was dried over Na_2SO_4, filtered, and concentrated to give phenyl *N*-(Benzyloxycarbonylamino)carbamate **1**. **1** (1.432 g, 5 mmol) and Phe-NHMe **2a** (980 mg, 1.1 equiv) (or Phe-NH_2 **2b**, 903 mg) were dissolved in chloroform (20 mL) and triethylamine (4.2 mL, 6 equiv) was added. The mixture was stirred for 7 days at rt. White precipitate was collected by filtration, washed with chloroform, 5 % citric acid, water, saturated $NaHCO_3$ and water. The product **3** was dried and *N*-protecting group was removed to give **4a**-**b**.



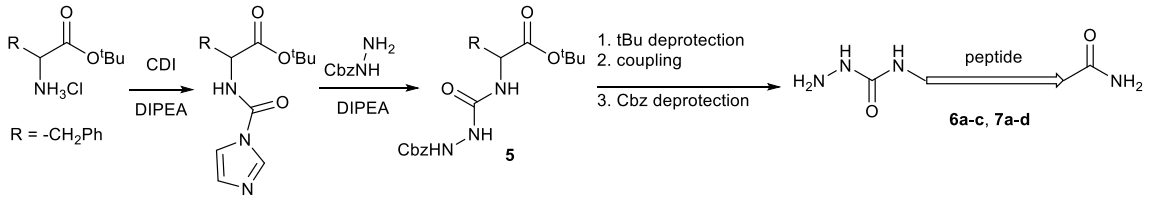
Synthesis of Cbz-AzaGly-PheOH 5'[4]

To a suspension of phenylalanine *tert*-butyl ester hydrochloride (10.0 mmol, 1.0 equiv) in DCM (20 mL) at 20 °C were added DIPEA (diisopropylethylamine, 2.5 equiv) and CDI (carbonyldiimidazole, 1.1 equiv). The reaction mixture was stirred for 2 hours at rt, and the organic layer was washed with water, $NaHCO_3$ and brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to give oily mono substituted imidazole derivative. This compound (1.0 equiv) was

dissolved in dry DCM (20 mL) and reacted with N^{α}-CBz-hydrazide (1.0 equiv) in the presence of DIPEA (1.0 equiv) at 20 °C overnight. The reaction mixture was poured into a separatory funnel, washed with water, 1 M HCl, brine solution, dried over $MgSO_4$, and evaporated under reduced pressure to give Cbz-AzaGly-Phe-O^{t}Bu **5**. **5** was dissolved in trifluoroacetic acid (20 mL) and stirred for 3 hours at rt. After completion of the reaction TFA was evaporated and 30 mL of ethyl acetate was added. White precipitate of **5'** was collected by filtration and dried.

General coupling procedure

Peptides were synthesized according to the standard protocols for the solution synthesis.[5] To *N*-protected amino acid or peptide in THF (od DMF for tripeptides) was added Oxyma (1.1 equiv). The mixture was vigorously stirred and cooled to 0°C. Then, amide of amino acid or peptide (1 equiv), triethylamine (1.1 equiv) and EDCI (1.1 equiv) was added to the solution. After 1 hour, the ice bath was removed and the reaction stirred at room temperature overnight. Solvents were evaporated under reduced pressure and the residues were suspended in water. The precipitate was collected by filtration, washed with water, saturated aqueous solution of NaHCO3, 5% citric acid and again water. The product was dried and *N*-protecting group was removed.

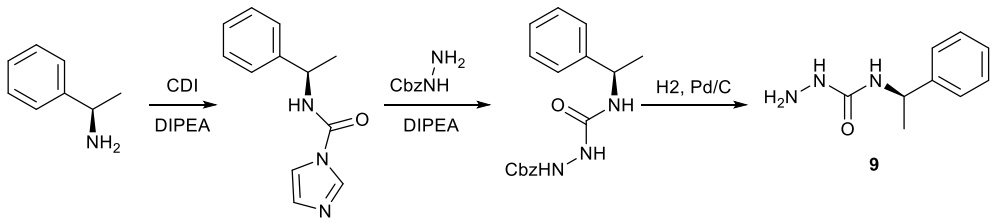


General CBz removal procedure

To the suspension of *N*-protected azapeptide in methanol under argon, palladium on activated charcoal was added (10% Pd basis, 50 mg per 1 mmol of azapeptide). Hydrogen from the balloon was bubbled through the solution at room temperature to complete conversion. The catalyst was removed by filtration through celite, the filtrate was concentrated under reduced pressure and dried.

Synthesis of AzaGly-(*R*)-1-phenylethylamine 9

To a solution of (*R*)-1-phenylethylamine (10.0 mmol, 1.0 equiv) in DCM (20 mL) at 20 °C were added DIPEA (diisopropylethylamine, 1.2 equiv) and CDI (carbonyldiimidazole, 1.1 equiv). The reaction mixture was stirred for 2 hours at rt, and the organic layer was washed with water, $NaHCO_3$ and brine solution. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to give oily mono substituted imidazole derivative. This compound (1.0 equiv) was dissolved in dry DCM (20 mL) and reacted with N^{α}-CBz-hydrazide (1.0 equiv) in the presence of DIPEA (1.0 equiv) at 20 °C overnight. The reaction mixture was poured into a separatory funnel, washed with water, 1 M HCl, brine solution, dried over $MgSO_4$, and evaporated under reduced pressure to give Cbz-AzaGly-(*R*)-1-phenylethylamine. To the solution of Cbz-AzaGly-(*R*)-1-phenylethylamine in methanol under argon, palladium on activated charcoal was added (10% Pd basis, 50 mg per 1 mmol). Hydrogen from the balloon was bubbled through the solution at room temperature to complete conversion. The catalyst was removed by filtration through celite, the filtrate was concentrated under reduced pressure and dried.



Synthesis of capsules and cavitands

Synthesis of capsules $(10b)_2$, $(11b)_2$, $(11c)_2$, (11a)(11b), $(12a)_2$, 12c

To tetraformylresorcin[4]arene **8** (0.1 mmol, 82.4 mg) in chloroform (4 ml) was added azapeptide (0.4 mmol). The reaction was stirred for 24 hours at 70° C in a sealed tube, washed with 5% citric acid, dried over anhydrous magnesium sulfate, filtered and evaporated to dryness. The resulting sample was analysed by NMR.

Synthesis of cavitands 10a, 11a, 12b, 12d

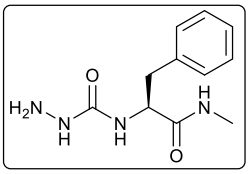
To tetraformylresorcin[4]arene **8** (0.1 mmol, 82.4 mg) in methanol (4 ml) was added azapeptide (0.4 mmol). The reaction was stirred for 24 hours at 70° C in a sealed tube and evaporated to dryness. If the product precipitated from methanol the precipitate was collected by filtration and dried. The resulting sample was analysed by NMR.

Synthesis of cavitand 13

To tetraformylresorcin[4]arene **8** (0.1 mmol, 82.4 mg) in chloroform (4 ml) was added azapeptide **9** (0.4 mmol). The reaction was stirred for 24 hours at 70° C in a sealed tube. The product, which precipitated from chloroform, was collected by filtration and dried. The resulting sample was analysed by NMR.

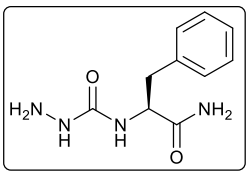
Analytical data for compounds

4a AzaGly-L-PheNHMe



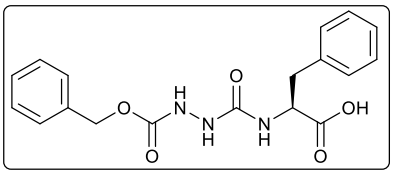
Yield (after 3 steps) 61 %
$[\alpha]_D^{22}$ + 12.3 ± 0.7 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 55.6; H, 6.8; N, 23.3. Calc. for $C_{11}H_{16}N_4O_2$: C, 55.9; H, 6.8; N, 23.7 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.87 (q, 1H, *J* = 4.6 Hz), 7.1-7.28 (m, 5H + s, 1H), 6.5 (d, 1H, *J* = 8.0 Hz), 4.43 (br s, 2H), 4.34 (ddd, 1H, J_1 = 5.6 Hz, J_2 = 8.0 Hz, J_3 = 8.1 Hz), 2.91 (dd, 1H, J_1 = 5.6 Hz, J_2 = 13.6 Hz), 2.81 (dd, 1H, J_1 = 8.1 Hz, J_2 = 13.6 Hz), 2.55 (d, 3H, *J* = 4.6 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 172.1, 159.4, 137.9, 129.2, 128.1, 126.2, 54.1, 38.8, 25.5.
HR MS (ESI): m/z calc for $[C_{11}H_{16}N_4O_2Na]^+$ 259.1171, found 259.1162 (|Δ| = 3.5 ppm)

4b AzaGly-L-PheNH$_2$



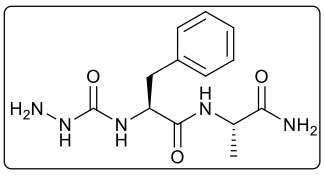
Yield (after 3 steps) 60 %
$[\alpha]_D^{22}$ + 13.8 ± 0.2 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 53.9; H, 6.3; N, 24.8. Calc. for $C_{10}H_{14}N_4O_2$: C, 54.0; H, 6.3; N, 25.2 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40 (br s, 1H), 7.16-7.28 (m, 5H), 7.02 (s, 1H), 7.00 (br s, 1H), 6.44 (br d, 1H, *J* = 7.2 Hz), 4.35 (ddd, 1H, J_1 = 7.2 Hz, J_2 = 5.3 Hz, J_3 = 7.9 Hz), 4.05 (br s, 2H), 2.95 (dd, 1H, J_1 = 5.3 Hz, J_2 = 13.8 Hz), 2.83 (dd, 1H, J_1 = 7.9 Hz, J_2 = 13. 8 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 173.7, 159.4, 137.9, 129.2, 128.0, 126.2, 53.7, 38.6.
HR MS (ESI): m/z calc for $[C_{10}H_{14}N_4O_2Na]^+$ 245.1014, found 245.1005 (|Δ| = 3.7 ppm)

5' Cbz-AzaGly-L-PheOH



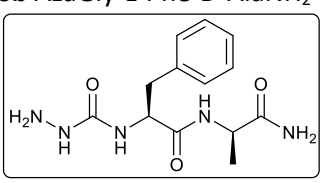
Yield (after 3 steps) 80 %
$[\alpha]_D^{22}$ + 35.6 ± 0.2 (c 0.01 gcm^{-3} in DMSO)
Elemental analysis Found: C, 60.4; H, 5.2; N, 11.5. Calc. for $C_{18}H_{19}N_3O_5$: C, 60.5; H, 5.4; N, 11.8 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.71 (br s, 1H), 8.95 (br s, 1H), 7.97 (br s, 1H), 7.16-7.38 (m, 10H), 6.33 (d, 1H, *J* = 8.1 Hz), 5.06 (s, 2H), 4.38 (ddd, 1H, J_1 = 8.1 Hz, J_2 = 5.2 Hz, J_3 = 7.3 Hz), 3.01 (dd, 1H, J_1 = 5.2 Hz, J_2 = 13.8 Hz), 2.94 (dd, 1H, J_1 = 7.3 Hz, J_2 = 13.8 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 173.3, 157.4, 156.6, 137.2, 136.7, 129.3, 128.3, 128.1, 127.9, 127.7, 126.4, 65.8, 53.7, 37.3.
HR MS (ESI): m/z calc for $[C_{18}H_{19}N_3O_5Na]^+$ 380.1222, found 380.1210 (|Δ| = 3.2 ppm)

6a AzaGly-L-Phe-L-AlaNH$_2$



$[\alpha]_D^{22}$ 3.1 ± 0.3 (c 0.01 gcm^{-3} in DMSO)
Elemental analysis Found: C, 53.0; H, 6.4; N, 23.5. Calc. for $C_{13}H_{19}N_5O_3$: C, 53.2; H, 6.5; N, 23.9 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.00 (d, 1H, *J* = 7.6), 7.14-7.28 (m, 5H + s, 1H), 7.08 (s, 1H), 6.97 (br s, 1H), 6.44 (br d, 1H), 4.39 (m, 1H), 4.20 (dq, 1H, J_1 = 7.6 Hz, J_2 = 7.1 Hz), 4.05 (br s, 2H), 2.98 (dd, 1H, J_1 = 4.8 Hz, J_2 = 13.8 Hz), 2.83 (dd, 1H, J_1 = 8.3 Hz, J_2 = 13.8 Hz), 1.21 (d, 3H, *J* = 7.1 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 174.0, 171.4, 159.5, 137.7, 129.3, 128.0, 126.2, 54.0, 47.9, 38.2, 18.3.
HR MS (ESI): m/z calc for $[C_{13}H_{19}N_5O_3Na]^+$ 316.1386, found 316.1374 (|Δ| = 3.8 ppm)

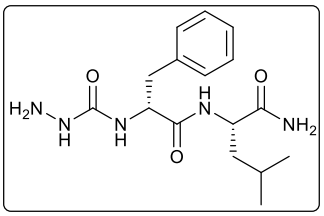
6b AzaGly-L-Phe-D-AlaNH$_2$



$[\alpha]_D^{22}$ + 24.8 ± 0.4 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 52.8; H, 6.5; N, 23.6. Calc. for $C_{13}H_{19}N_5O_3$: C, 53.2; H, 6.5; N, 23.9 %

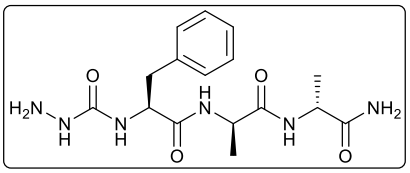
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08 (d, 1H, *J*= 7.8 Hz), 7.13-7.31 (m, 5H + s, 1H + s, 1H), 6.96 (br s, 1 H), 6.51 (d, 1H, *J* = 7.0), 4.36 (ddd, 1H, J_1 = 5.9 Hz, J_2 = 8.0 Hz, J_3 = 7.0 Hz), 4.31 (br s, 2H), 4.13 (dq, 1H, J_1 = 7.2 Hz, J_2 = 7.8 Hz), 2.91 (dd, 1H, J_1 = 5.9 Hz, J_2 = 13.6 Hz), 2.85 (dd, 1H, J_1 = 8.0 Hz, J_2 = 13.6 Hz), 1.11 (d, 3H, *J* = 7.2 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 174.1, 171.3, 159.5, 137.6, 129.2, 128.0, 126.2, 54.3, 47.8, 38.3, 17.9.
HR MS (ESI): m/z calc for $[C_{13}H_{19}N_5O_3Na]^+$ 316.1386, found 316.1378 (|Δ| = 2.5 ppm)

6c AzaGly-D-Phe-L-LeuNH_2



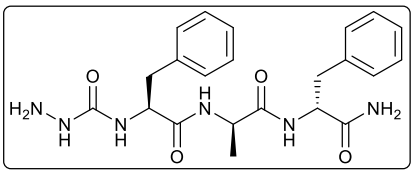
$[\alpha]_D^{22}$ – 40.8 ± 0.05 (c 0.01 gcm^{-3} in DMF)
Elemental analysis Found: C, 57.3; H, 7.5; N, 20.7. Calc. for $C_{16}H_{25}N_5O_3$: C, 57.3; H, 7.5; N, 20.9 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.09 (s, 1H, *J* = 8.4 Hz), 7.34 (s, 1H), 7.16-7.27 (m, 5H), 7.12 (s, 1H), 6.92 (s, 1H), 6.49 (br d, 1H), 4.35-4.41 (m, 1H), 4.04-4.12 (m, 1H + br s, 2H), 2.80-2.94 (m, 2H), 1.30-1.44 (m, 2H), 1.19-1.27 (m, 1H), 0.78 (d, 3H, *J* = 6.5 Hz), 0.72 (d, 3H, *J* = 6.4 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 174.3, 171.7, 159.7, 137.4, 129.2, 128.1, 126.2, 54.5, 50.8, 38.4, 23.9, 23.2, 21.2.
HR MS (ESI): m/z calc for $[C_{16}H_{25}N_5O_3Na]^+$ 358.1855, found 358.1848 (|Δ| = 2.0 ppm)

7a AzaGly-L-Phe-D-Ala-D-AlaNH_2



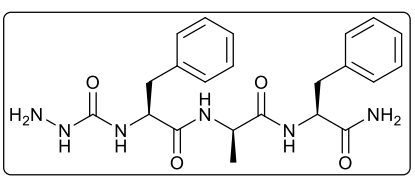
$[\alpha]_D^{22}$ + 67.8 ± 0.8 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 52.4; H, 6.6; N, 22.7. Calc. for $C_{16}H_{24}N_6O_4$: C, 52.7; H, 6.6; N, 23.1 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.30 (d, 1H, *J* = 7.0 Hz), 7.89 (d, 1H, *J* = 7.8 Hz), 7.17-7.30 (m, 5H), 7.13 (s, 1H), 7.00 (br s, 1H), 6.93 (br s, 1H), 6.49 (br d, 1H), 4.35 (m, 1H), 4.13 (m, 1H + 1H), 2.91 (dd, 1H, J_1 = 5.9 Hz, J_2 = 13.6 Hz), 2.85 (dd, 1H, J_1 = 8.2 Hz, J_2 = 13.6 Hz), 1.23 (d, 3H, *J* = 7.2 Hz), 1.14 (d, 3H, *J* = 7.2 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 174.3, 172.3, 171.6, 159.7, 137.5, 129.2, 128.1, 126.3, 54.4, 48.6, 48.2, 38.1, 17.8, 17.5.
HR MS (ESI): m/z calc for $[C_{16}H_{24}N_6O_4Na]^+$ 387.1757, found 387.1749 (|Δ| = 2.1 ppm)

7b AzaGly-L-Phe-D-Ala-D-PheNH_2



$[\alpha]_D^{22}$ + 52.4 ± 0.1 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 59.7; H, 6.3; N, 18.8. Calc. for $C_{22}H_{28}N_6O_4$: C, 56.0; H, 6.4; N, 19.1 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (d, 1H, *J* = 6.7 Hz), 7.92 (d, 1H, *J* = 8.5 Hz), 7.15-7.30 (m, 10H + s, 1H), 7.05 (s, 1H + s, 1H), 6.51 (br d, 1H), 4.26-4.37 (m, 1H + 1H), 4.13 (br s, 2H), 4.01 (dq, 1H, J_1 = 6.7 Hz, J_2 = 7.2 Hz), 3.05 (dd, 1H, J_1 = 4.4 Hz, J_2 = 13.8 Hz), 2.80-2.94 (m, 1H + 1H +1H), 1.02 (d, 3H, *J* = 7.2 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 173.1, 172.6, 171.8, 159.9, 138.3, 137.5, 129.2, 129.0, 128.1, 128.0, 126.3, 126.1, 54.5, 54.2, 48.9, 37.9, 36.9, 17.3.
HR MS (ESI): m/z calc for $[C_{22}H_{28}N_6O_4Na]^+$ 463.2070, found 463.2061 (|Δ| = 1.9 ppm)

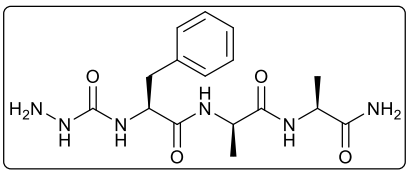
7c AzaGly-L-Phe-D-Ala-L-PheNH_2



$[\alpha]_D^{22}$ + 28.7 ± 0.1 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 59.7; H, 6.5; N, 18.8. Calc. for $C_{22}H_{28}N_6O_4$: C, 56.0; H, 6.4; N, 19.1 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (d, 1H, *J* = 8.7 Hz), 8.07 (d, 1H, *J* = 7.5 Hz), 7.34 (s, 1H), 7.09-7.27 (m, 10 H + s, 1H + s, 1H), 6.50 (br d, 1H), 4.33-4.41 (m, 1H + 1H), 4.15 (dq, 1H, 1H, J_1 = 7.1 Hz, J_2 = 7.5 Hz), 4.12 (br s, 2H), 3.05

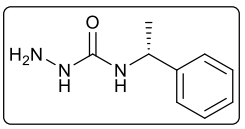
(dd, 1H, J_1 = 4.2 Hz, J_2 = 13.6 Hz), 2.82-2.93 (m, 1H + 1H), 2.76 (dd, 1H, J_1 = 10.5 Hz, J_2 = 13.6 Hz), 0.90 (d, 3H, J = 7.1 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 173.0, 171.7, 171.4, 159.5, 138.2, 137.6, 129.2, 129.1, 128.0, 127.9, 126.2, 126.1, 54.2, 53.9, 48.0, 38.5, 37.4, 17.8.
HR MS (ESI): m/z calc for $[C_{22}H_{28}N_6O_4Na]^+$ 463.2070, found 463.2062 (|Δ| = 1.7 ppm)

7d AzaGly-L-Phe-D-Ala-L-AlaNH_2



$[\alpha]_D^{22}$ + 33.3 ± 0.4 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 52.5; H, 6.6; N, 23.0. Calc. for $C_{16}H_{24}N_6O_4$: C, 52.7; H, 6.6; N, 23.1 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.17 (d, 1H, J = 7.4 Hz), 8.00 (d, 1H, J = 7.8 Hz), 7.16-7.29 (m, 5H + s, 1H), 7.11 (s, 1H), 6.97 (s, 1H), 6.51 (br d, 1H), 4.35 (m, 1H), 4.08-4.23 (m, 1H+ 1H + br s, 2H), 2.91 (dd, 1H, J_1 = 6.0 Hz, J_2 = 13.6 Hz), 2.85 (dd, 1H, J_1 = 7.9 Hz, J_2 = 13.6 Hz), 1.20 (d, 3H, J = 7.2 Hz), 1.11 (d, 3H, J = 7.1 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 174.2, 171.63, 171.60, 159.6, 137.6, 129.2, 128.1, 126.3, 54.4, 48.2, 48.1, 38.3, 18.0, 17.7.
HR MS (ESI): m/z calc for $[C_{16}H_{24}N_6O_4Na]^+$ 387.1757, found 387.1743 (|Δ| = 3.6 ppm)

9 AzaGly-(*R*)-1-phenylethylamine



Yield (after 3 steps) 70 %
$[\alpha]_D^{22}$ + 11.4 ± 1.1 (c 0.01 gcm^{-3} in methanol)
Elemental analysis Found: C, 60.6; H, 7.4; N, 23.0. Calc. for $C_9H_{13}N_3O$: C, 60.3; H, 7.3; N, 23.4 %
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.18-7.33 (m, 5H), 6.93 (s, 1H), 6.59 (d, 1H, J = 8.2 Hz), 4.74-4.83 (m, 1H), 4.09 (s, 2H), 1.36 (d, 3H, J = 7.0 Hz).
^{13}C NMR (100 MHz, DMSO-d_6): δ 159.4, 145.6, 128.1, 126.4, 125.8, 48.2, 23.1.
HR MS (ESI): m/z calc for $[C_9H_{13}N_3ONa]^+$ 202.0956, found 202.0939(|Δ| = 8.4 ppm)

Analytical data for cavitands and capsules

10a

Yield 69 % (precipitate from methanol)

$[\alpha]_D^{22}$ + 77.0 ± 0.1 (c 0.006 gcm^{-3} in DMF)

^{1}H NMR (600 MHz, DMSO-d$_6$): δ 10.64 (br s, 4H, *OH*), 10.29 (s, 4H, *g*), 10.02 (br s, 4H, *OH*), 8.34 (s, 4H, *f*), 7.95 (q, 4H, *J* = 4.4 Hz, *l*), 7.43 (s, 4H, e_1), 7.14-7.27 (m, 20H, *k*), 6.71 (d, 4H, *J* = 6.5 Hz, *h*), 4.57 (t, 4H, *J* = 7.0 Hz, *d*), 4.33-4.37 (m, 4H, *i*), 3.00 (dd, 4H, J_1 = 4.5 Hz, J_2 = 13.4 Hz, j_1), 2.87 (dd, 4H, J_1 = 9.0 Hz, J_2 = 13.4 Hz, j_2), 2.59 (d, 12H, *J* = 4.4 Hz, *m*), 2.04-2.10 (m, 8H, *c*), 1.35-1.41 (m, 4H, *b*), 0.94 (d, 24H, *J* = 6.4 Hz, *a*).

^{13}C NMR (150 MHz, DMSO-d$_6$): δ 171.8 (*o*), 153.7 (*n*), 151.12, 151.06 (e_3 + e_5), 141.0 (*f*), 137.9 (k_1), 129.2 (k_2), 128.1 (k_3), 127.0 (e_1), 126.3 (k_4), 123.6 (e_2 + e_6), 106.9 (e_4), 54.8 (*i*), 42.5 (*c*), 38.0 (*j*), 30.7 (*d*), 25.9 (*b*), 25.5 (*m*), 22.7 (*a*).

HR MS (ESI): m/z calc for $[C_{92}H_{112}N_{16}O_{16}Na]^+$ 1719.8340, found 1719.8334 (|Δ| = 0.3 ppm)

Diffusion coefficient obtained by DOSY 1.28 × 10^{-10} m^{2}s^{-1} in DMSO.

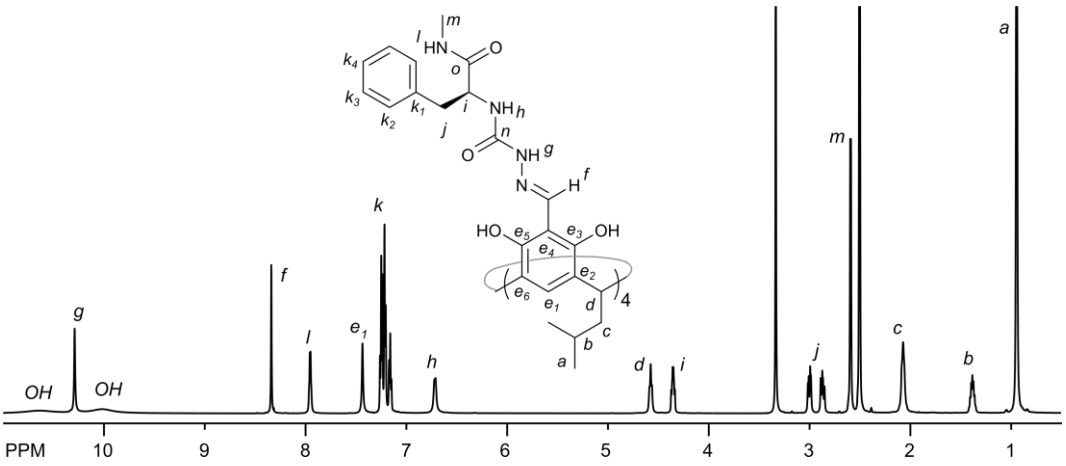


Figure S1. ^{1}H NMR spectrum of **10a** (DMSO-d$_6$, 600 MHz).

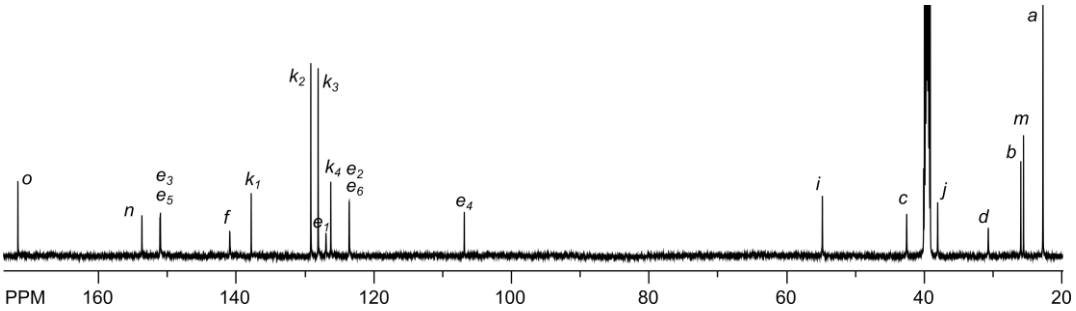


Figure S2. ^{13}C NMR spectrum of **10a** (DMSO-d$_6$, 150 MHz).

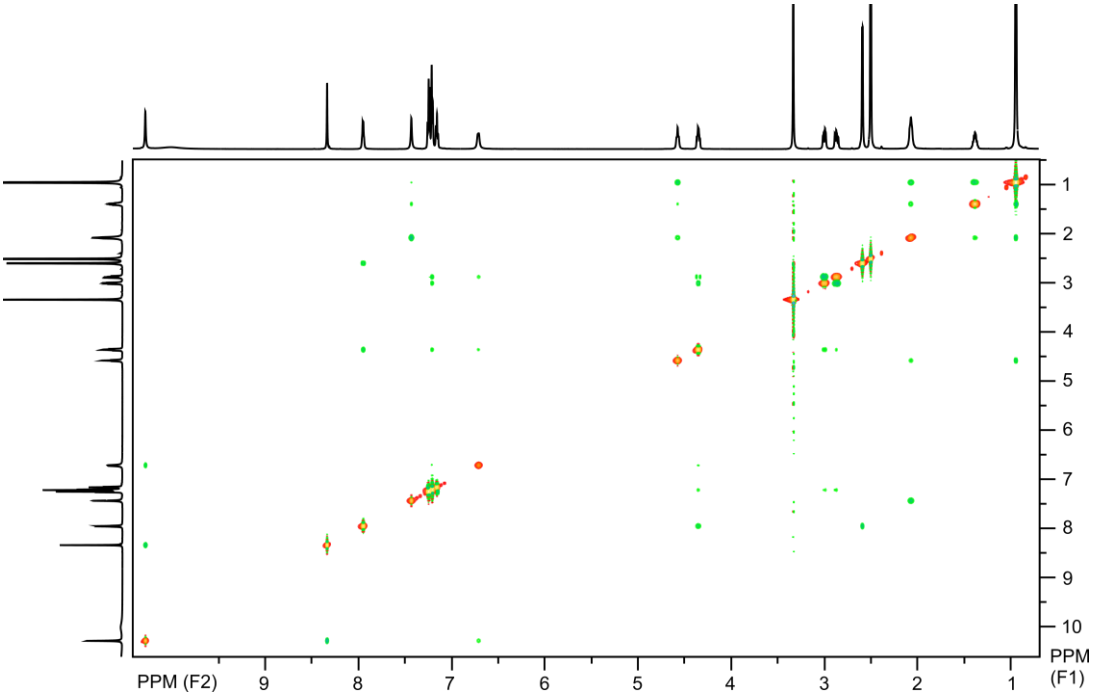


Figure S3. ROESY spectrum of **10a** (DMSO-d_6, 600 MHz).

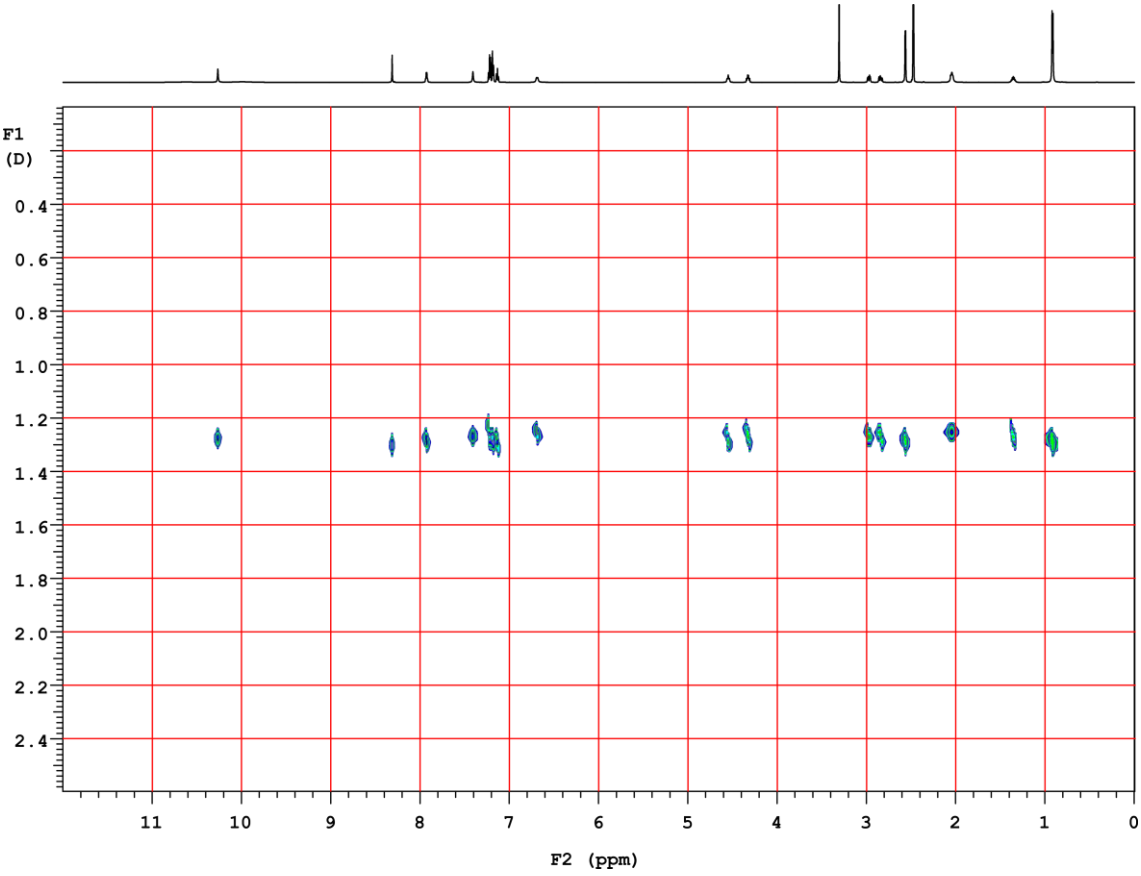


Figure S4. DOSY spectrum of **10a** (DMSO-d_6, 600 MHz).

$(10b)_2$

Yield 78 %

$[\alpha]_D^{22}$ + 26.7 ± 0.2 (c 0.009 gcm^{-3} in DMF)

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.56 (s, 4H, *e_5-OH*), 9.94 (s, 4H, *g*), 9.39 (s, 4H, *e_3-OH*), 8.56 (s, 4H, *f*), 8.29 (s, 4H, *l_2*), 7.26-7.33 (m, 20H, *k*), 7.15 (s, 4H, *e_1*), 6.00 (s, 4H, *l_1*), 5.47 (d, 4H, *J* = 7.7 Hz, *h*), 4.93 (ddd, 4H, J_1 = 7.7 Hz, J_2 = 4.9 Hz, J_3 = 5.9 Hz, *i*), 4.44 (t, 4H, *J* = 8.0 Hz, *d*), 3.25 (dd, 4H, J_1 = 4.9 Hz, J_2 = 13.8 Hz, j_1), 3.09 (dd, 4H, J_1 = 5.9 Hz, J_2 = 13.8 Hz, j_2), 2.10 (dd, 8H, J_1 = 8.0 Hz, J_2 = 6.9 Hz, *c*), 1.49-1.56 (m, 4H, *b*), 1.01 (d, 12H, *J* = 6.6 Hz, a_1), 1.00 (d, 12h, *J* = 6.6 Hz, a_2).

^{13}C NMR (150 MHz, $CDCl_3$): δ 174.5 (*n*), 153.8 (*m*), 151.4 (e_5), 151.3 (e_3), 143.3 (*f*), 136.2 (k_1), 129.9 (k_2), 128.3 (k_3), 127.0 (k_4), 125.2 *(e_1)*, 123.8 (e_2), 123.6 *(e_6)*, 107.1 (e_4), 53.9 (*i*), 41.4 (*c*), 40.9 (*j*), 30.6 (*d*), 26.1 (*b*), 22.7 (*a*).

HR MS (ESI): m/z calc for $[C_{88}H_{103}N_{16}O_{16}]^-$ 1639.7738, found 1639.7740 (|Δ| = 0.1 ppm)

Diffusion coefficient obtained by DOSY 3.35 × 10^{-10} m^{2}s^{-1} in chloroform.

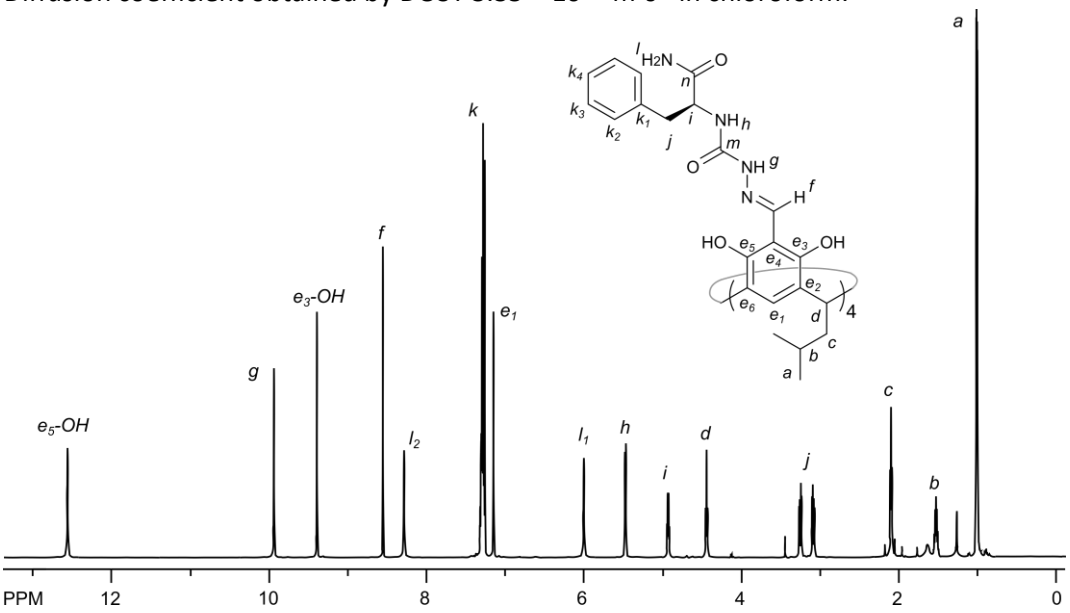


Figure S5. ^{1}H NMR spectrum of (**10b**)$_2$ ($CDCl_3$, 600 MHz).

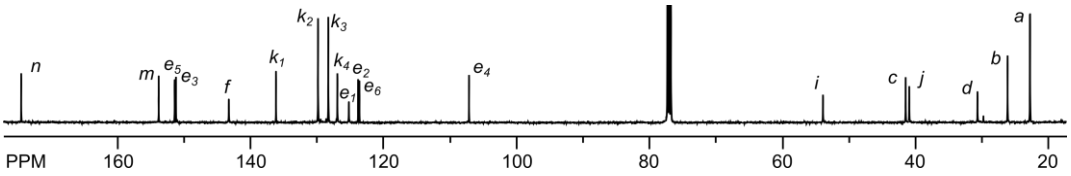


Figure S6. ^{13}C NMR spectrum of (**10b**)$_2$ ($CDCl_3$, 150 MHz).

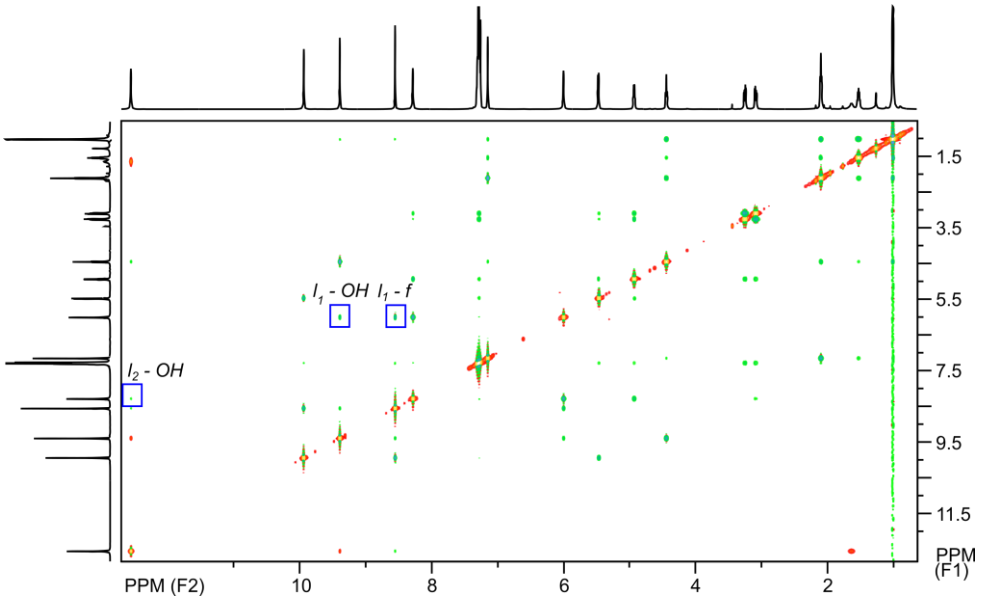


Figure S7. ROESY spectrum of (**10b**)$_2$ ($CDCl_3$, 600 MHz, most indicative signals in frames).

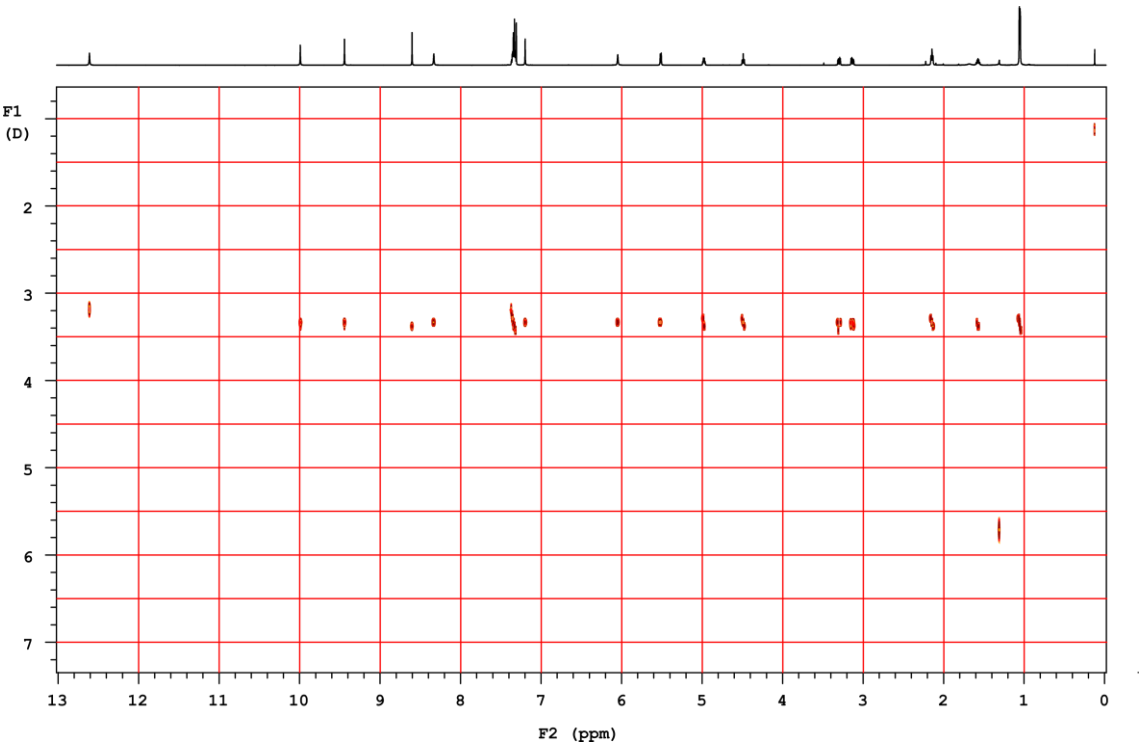


Figure S8. DOSY spectrum of (**10b**)$_2$ ($CDCl_3$, 600 MHz).

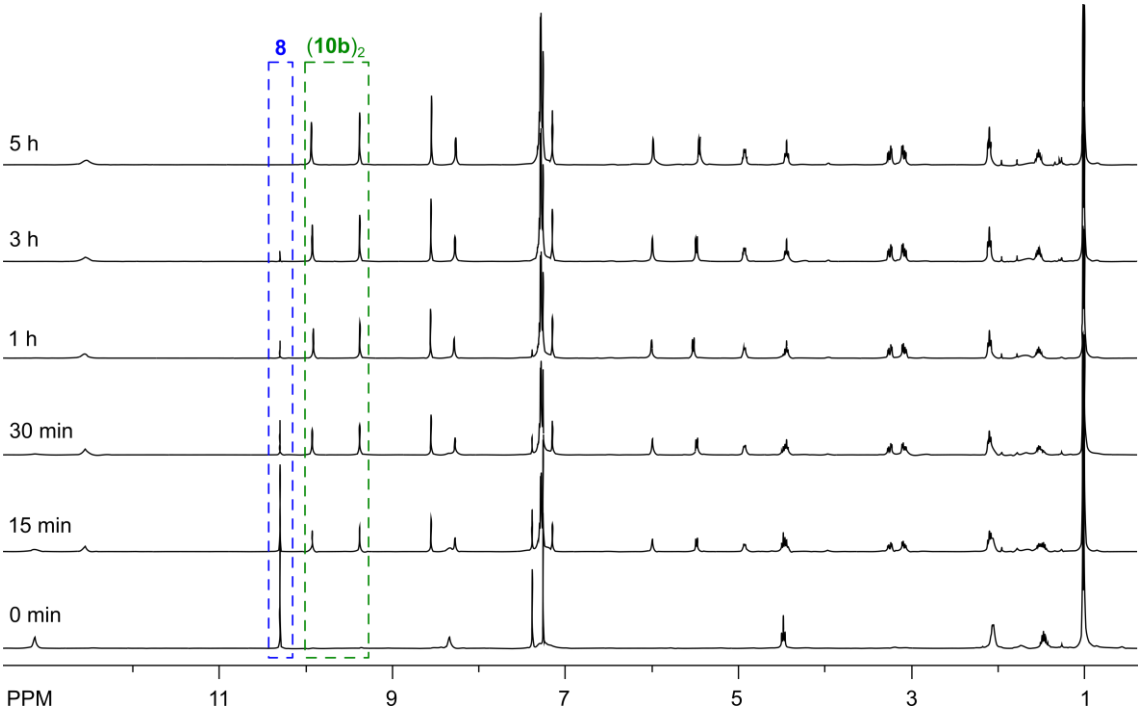


Figure S9. Reaction kinetics of **8** with L-**4b** ($CDCl_3$, 400 MHz).

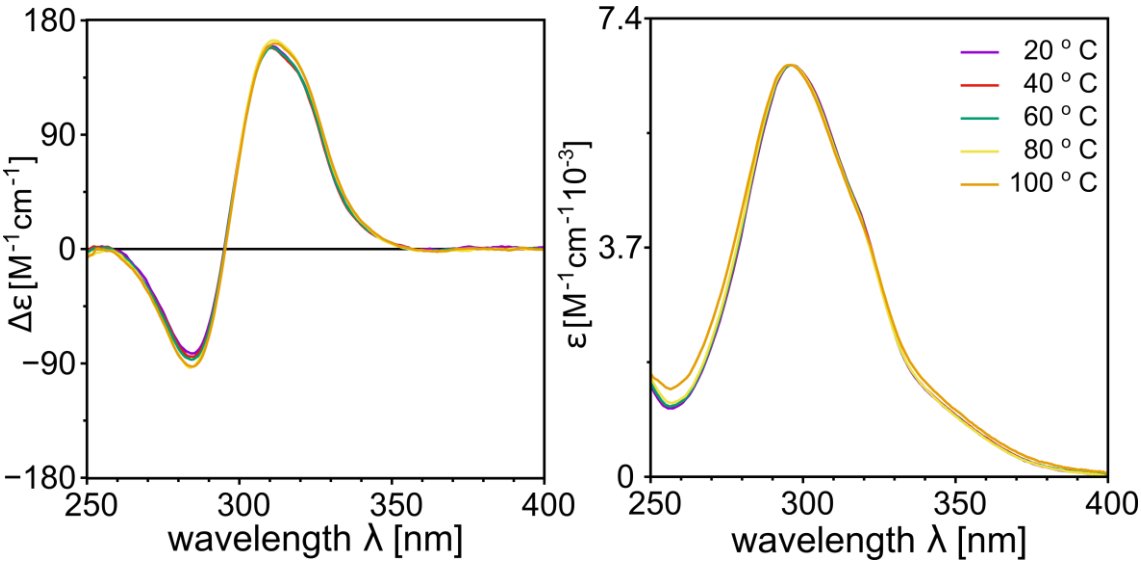


Figure S10. Temperature-dependent ECD and UV spectra of (**10b**)$_2$ in tetrachloroethane.

11a

Yield 67 % (precipitate from reaction in methanol)
$[\alpha]_D^{22}$ + 29.1 ± 0.3 (c 0.005 gcm^{-3} in DMF)
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 10.34 (s, 4H, *g*), 10.20 (br s, 8H, *OH*), 8.35 (s, 4H, *f*), 8.14 (d, 4H, J = 7.1 Hz, *l*), 7.43 (s, 4H, e_1), 7.14-7.27 (m, 20H, *k* + s, 4H, o_2), 7.02 (s, 4H, o_1), 6.71 (br s, 4H, *h*), 4.59 (br t, 4H, *d*), 4.41 (m, 4H, *i*), 4.21-4.27 (m, 4H, *m*), 3.03-3.08 (m, 4H, j_1), 2.84-2.89 (m, 4H, j_2), 2.03-2.09 (m, 8H, *c*), 1.35-1.41 (m, 4H, *b*), 2.23 (d, 12H, J = 7.0 Hz, *n*), 0.94 (d, 24H, J = 6.3 Hz, *a*).
^{13}C NMR (150 MHz, DMSO-d$_6$): δ 174.1 (*s*), 171.1 (*r*), 153.9 (*p*), 151.1 (e_3 + e_5), 141.2 (*f*), 137.8 (k_1), 129.3 (k_2), 128.1 (k_3), 127.1 (e_1), 126.3 (k_4), 123.6 (e_2 +e_6), 106.9 (e_4), 54.8 (*i*), 48.0 (*m*), 42.6 (*c*), 37.7 (*j*), 30.7 (*d*), 25.9 (*b*), 22.7 (*a*), 18.4 (*n*).
HR MS (ESI): m/z calc for $[C_{100}H_{124}N_{20}O_{20}Na]^+$ 1947.9198, found 1947.9225 (|Δ| = 1.4 ppm)
Diffusion coefficient obtained by DOSY 1.40 × 10^{-10} m^{2}s^{-1} in DMSO.

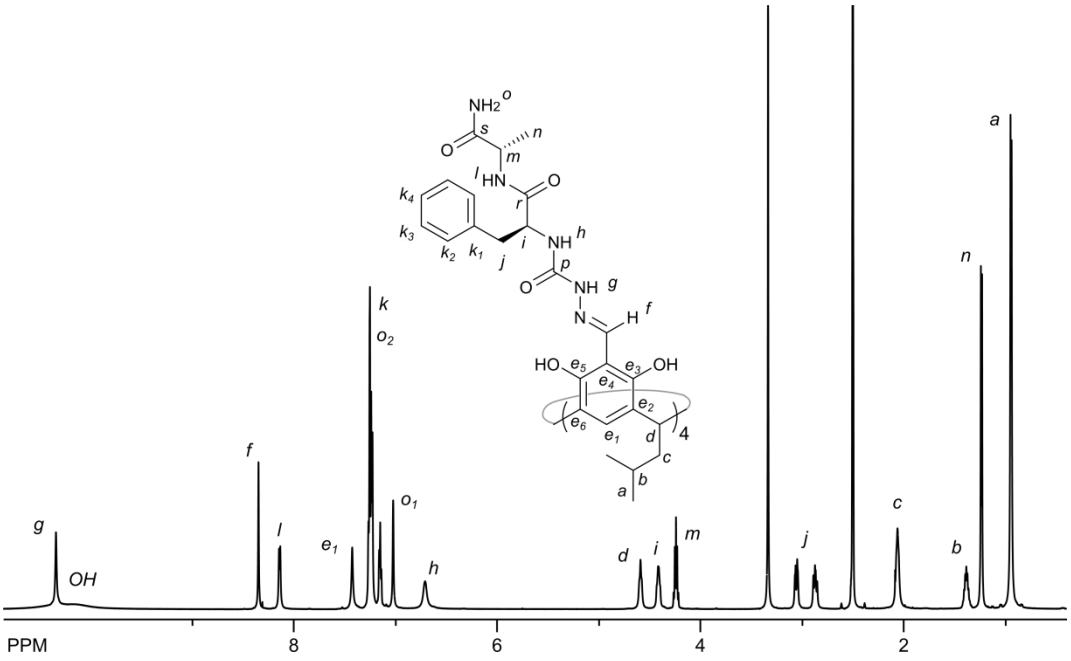


Figure S11. ^{1}H NMR spectrum of **11a** (DMSO-d$_6$, 600 MHz).

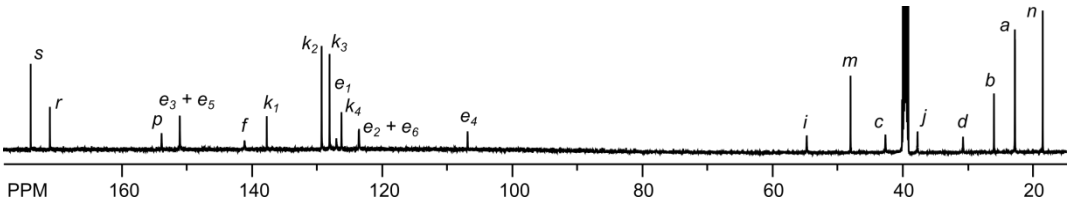


Figure S12. ^{13}C NMR spectrum of **11a** (DMSO-d$_6$, 150 MHz).

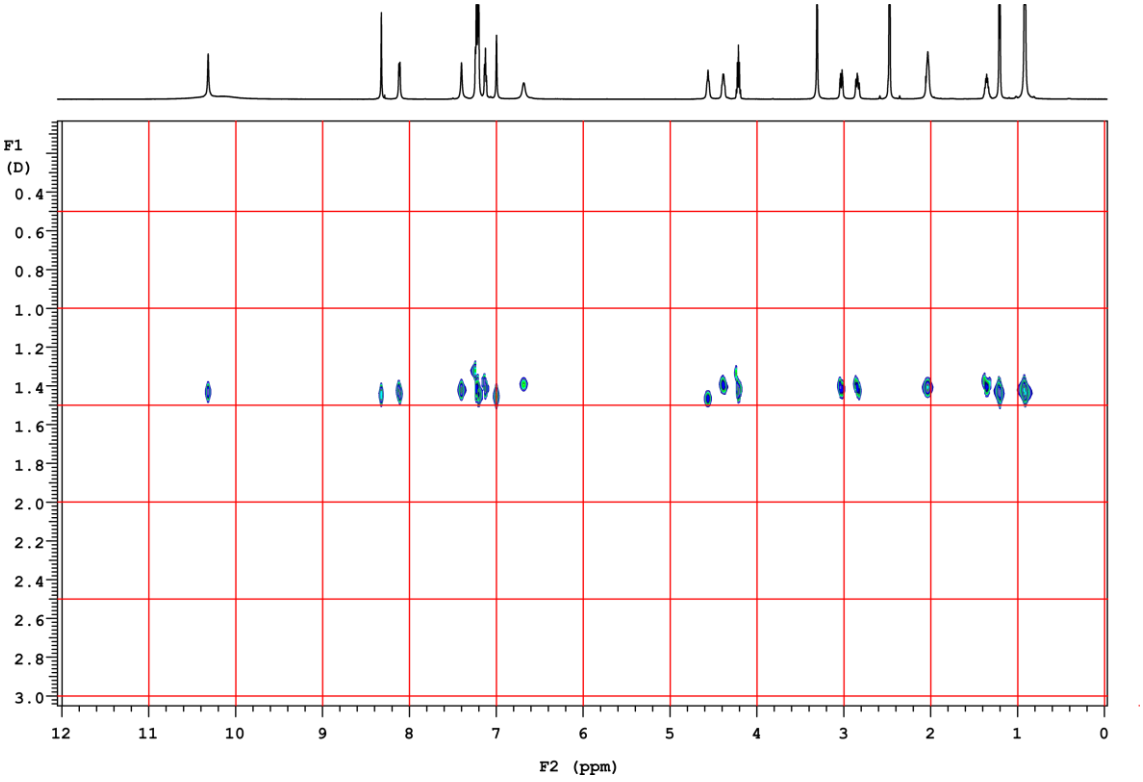


Figure S13. DOSY spectrum of **11a** (DMSO-d_6, 600 MHz).

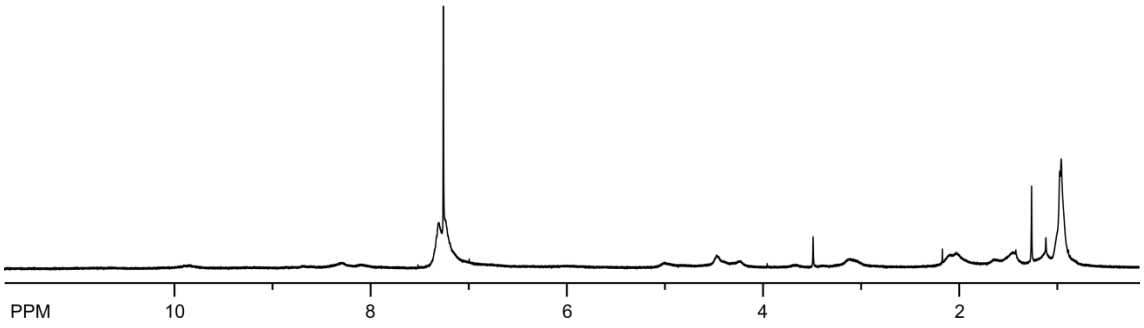


Figure S14. ^{1}H NMR spectrum of **11a** ($CDCl_3$, 400 MHz).

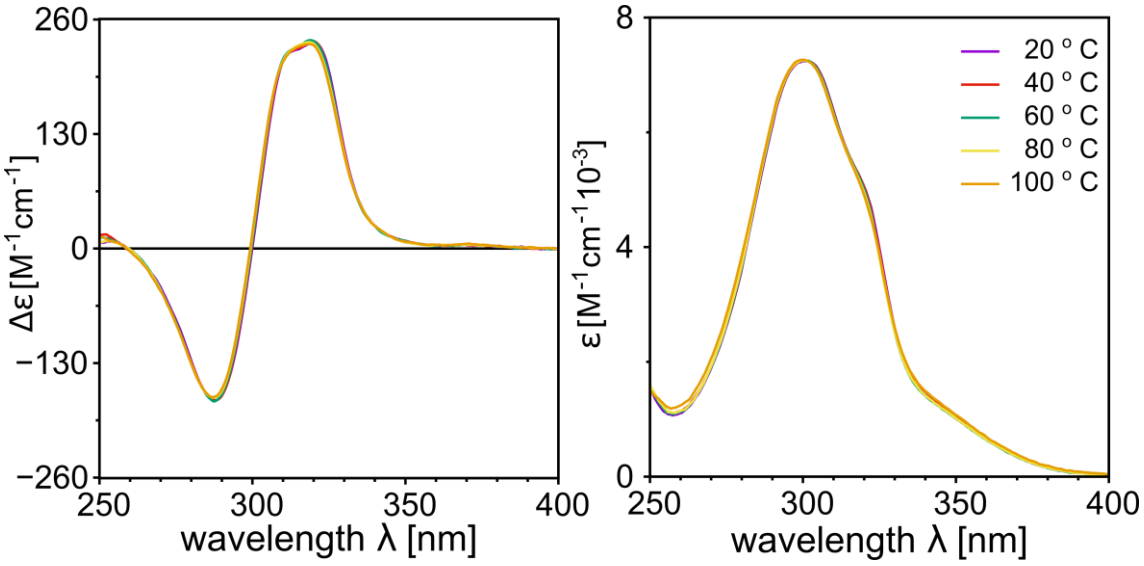


Figure S15. Temperature-dependent ECD and UV spectra of (**11a**)$_2$ in tetrachloroethane.

$(11b)_2$

Yield 65 %

$[\alpha]_D^{22}$ + 26.0 ± 0.3 (c 0.005 gcm^{-3} in DMF)

^{1}H NMR (600 MHz, $CDCl_3$): (broaden peaks, no coupling constants) δ 13.86 (s, 4H, e_5-*OH*), 10.04 (s, 4H, *g*), 8.81 (s, 4H, e_3-*OH*), 8.04 (s, 4H, *l* + s, 4H, *f*), 7.91 (s, 4H, o_2), 7.23-7.38 (m, 20H, *k* + s, 4H, *h*), 7.20 (s, 4H, e_1), 5.75 (s, 4H, o_1), 5.40 (m, 4H, *i*), 4.47 (br t, 4H, *d*), 4.09 (m, 4H, *m*), 3.08 (m, 4H, j_1), 2.93 (m, 4H, j_2), 2.11 (m, 4H, c_1), 1.99 9m, 4H, c_2), 1.45 (m, 4H, *b*), 0.97 (d, 24H, J = 6.1 Hz, *a*).

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.0 (*r*), 171.8 (*s*), 154.4 (*p*), 152.0, 150.8 (e_3 and e_5), 138.0 (*f*), 135.9 (k_1), 129.5 (k_2), 128.7 (k_3), 127.1 (k_4), 125.3 (e_1), 123.9, 123.3 (e_2 and e_6), 106.6 (e_4), 53.9 (*i*), 49.6 (*m*), 42.2 (*c*), 41.1 (*j*), 30.3 (*d*), 26.1 (*b*), 22.8 (a_1), 22.6 (a_2), 19.0 (*n*).

HR MS (ESI): m/z calc for $[C_{100}H_{122}N_{20}O_{20}]^{2-}$ 961.4567, found 961.4584 (|Δ| = 1.8 ppm)

Diffusion coefficient obtained by DOSY × 3.20 10^{-10} m^{2}s^{-1} in chloroform.

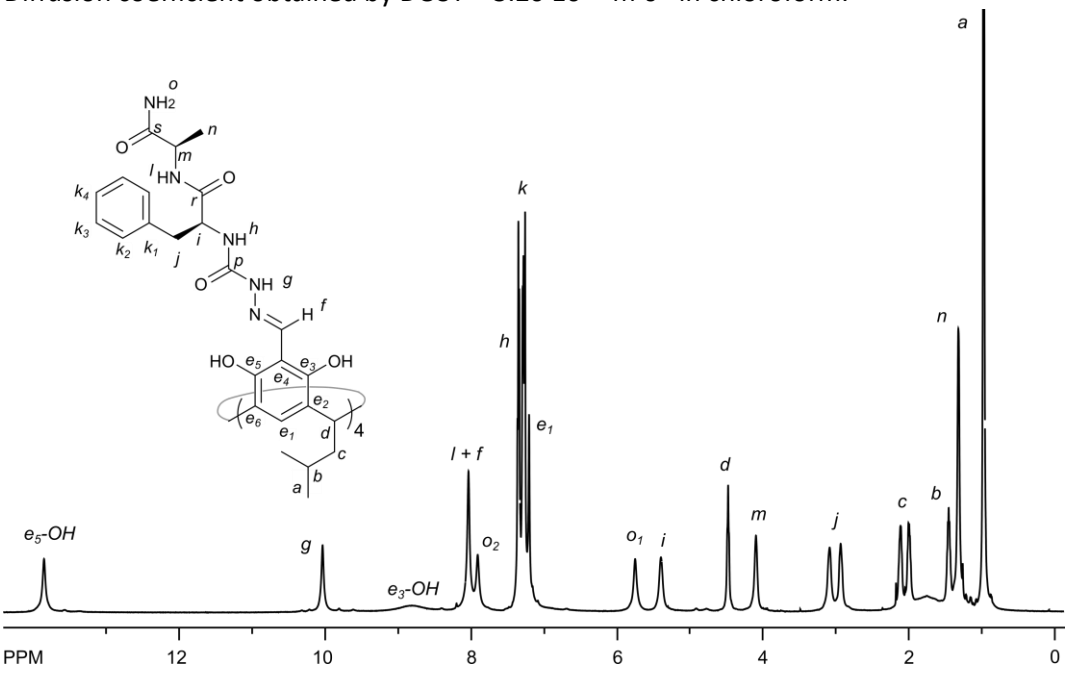


Figure S16. ^{1}H NMR spectrum of (**11b**)$_2$ ($CDCl_3$, 600 MHz).

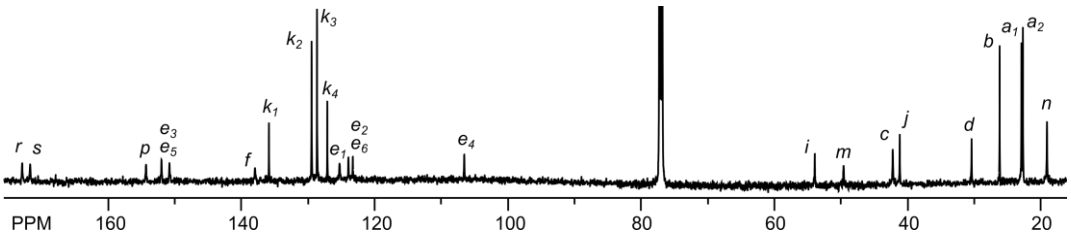


Figure S17. ^{13}C NMR spectrum of (**11b**)$_2$ ($CDCl_3$, 150 MHz).

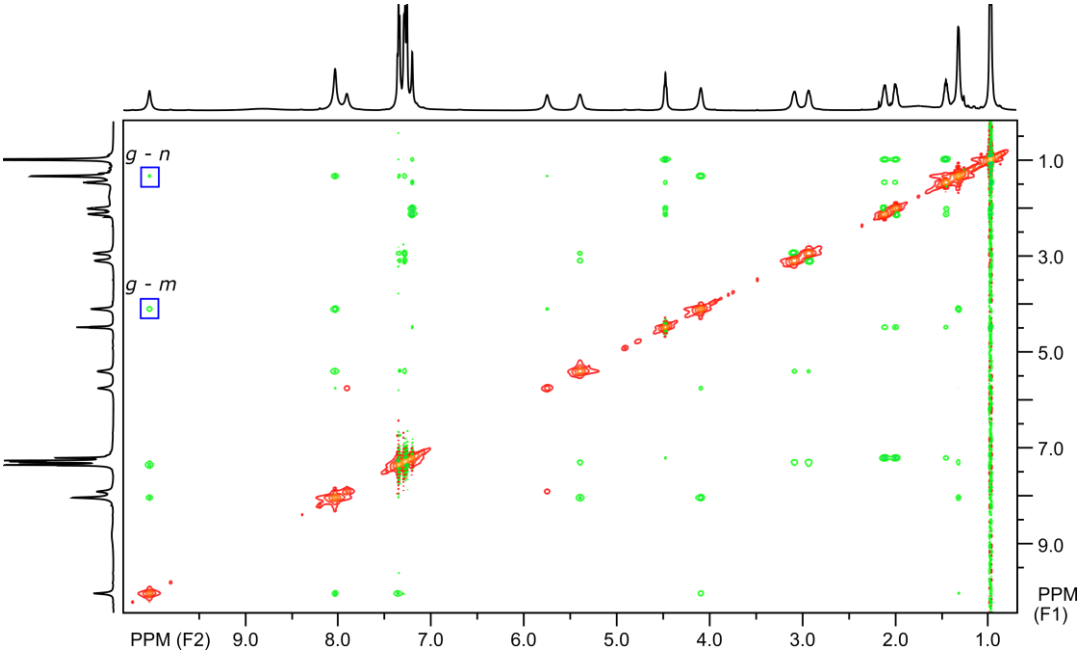


Figure S18. ROESY spectrum of (**11b**)$_2$ ($CDCl_3$, 600 MHz, most indicative signals in frames).

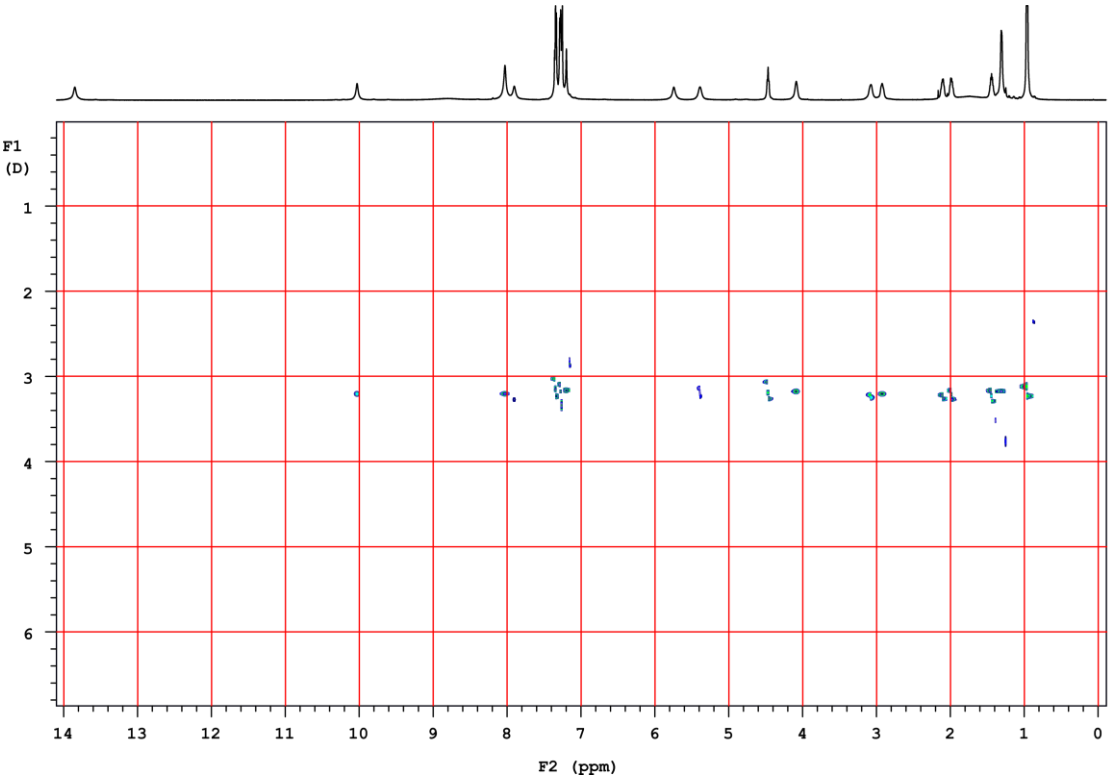


Figure S19. DOSY spectrum of (**11b**)$_2$ ($CDCl_3$, 600 MHz).

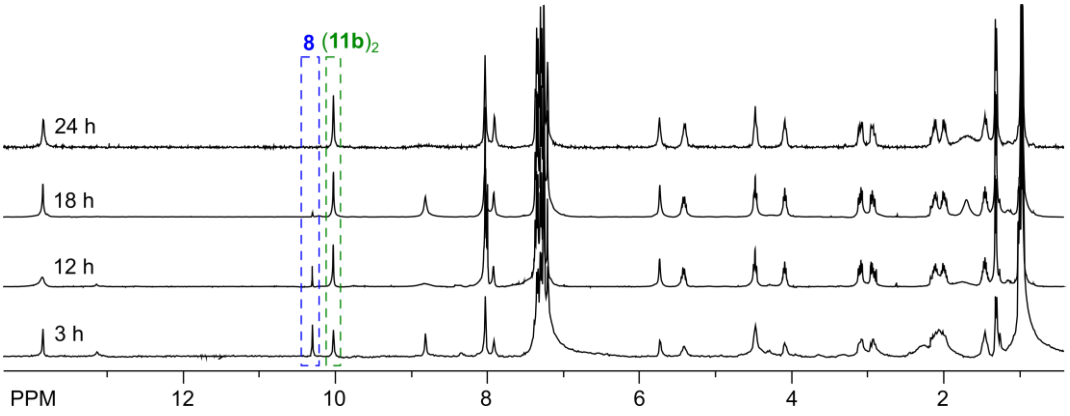


Figure S20. Reaction kinetics of **8** with (L,D)-**6b** ($CDCl_3$, 400 MHz).

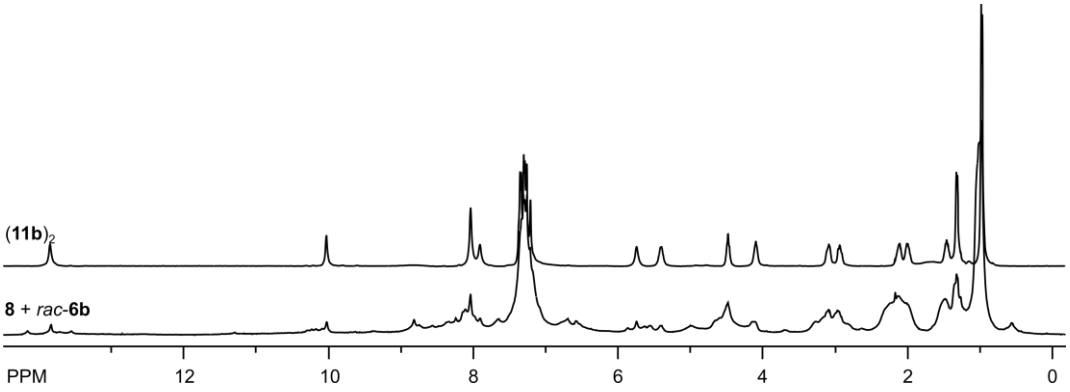


Figure S21. Chiral self-sorting of peptides in reaction of **8** with *rac*-**6b** (^{1}H NMR spectra, $CDCl_3$, 400 MHz).

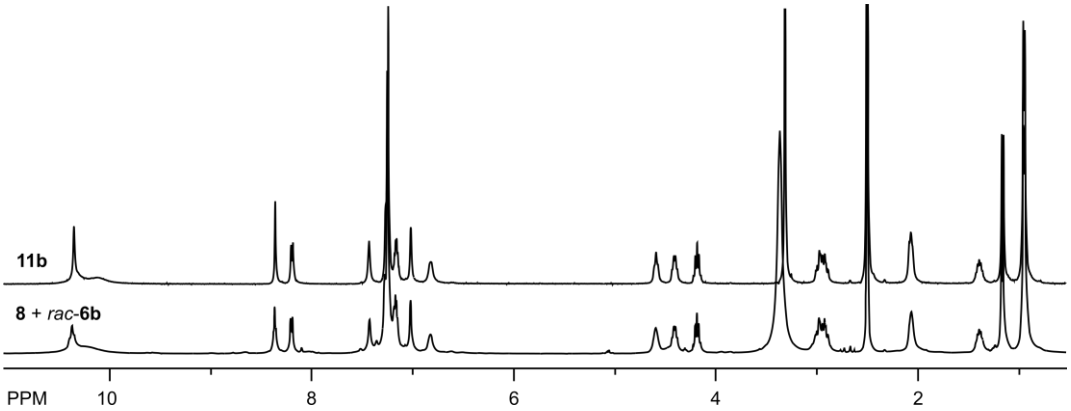


Figure S22. Chiral self-sorting of peptides in reaction of **8** with *rac*-**6b** (^{1}H NMR spectra, DMSO-d_6, 400 MHz).

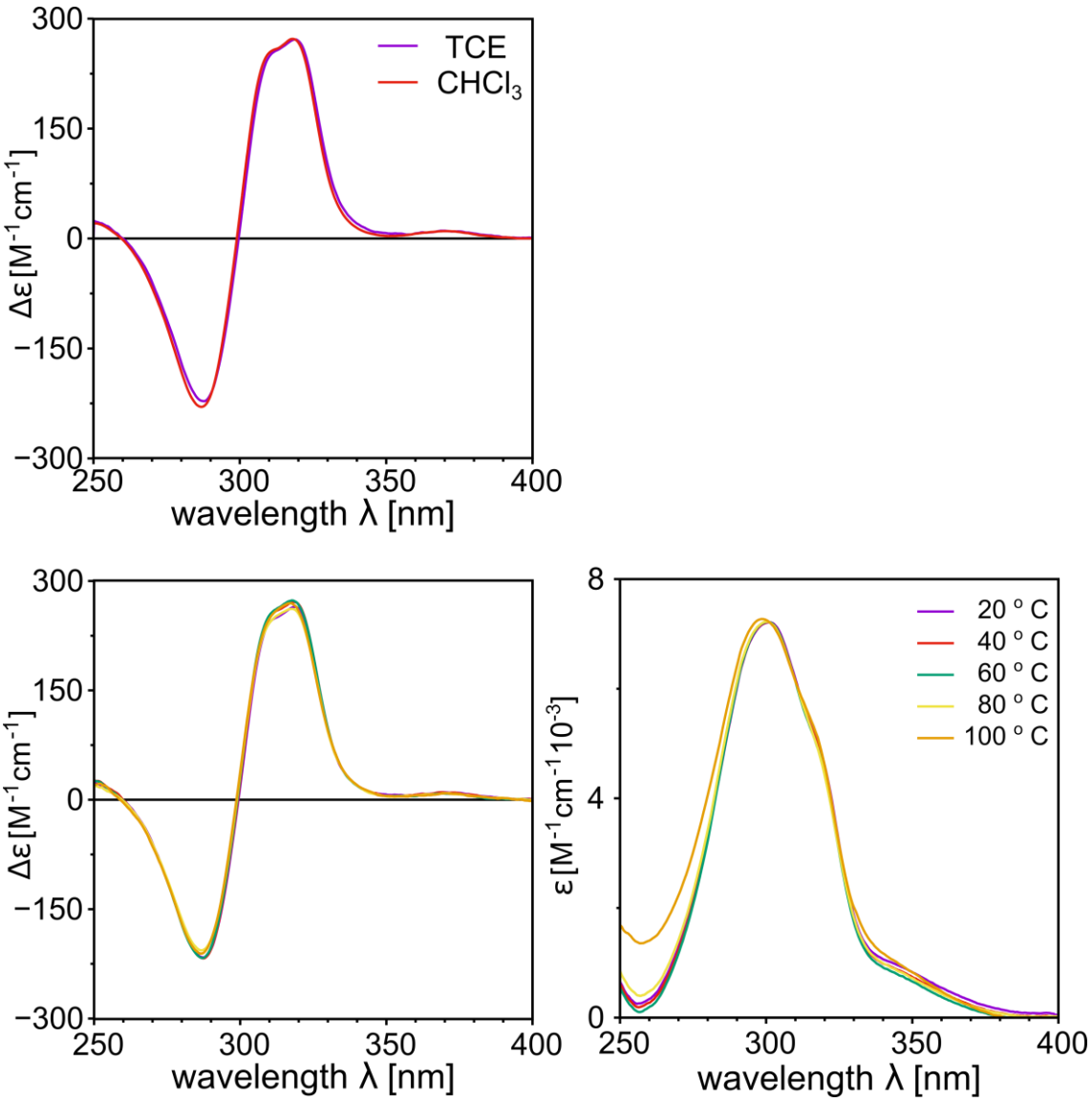


Figure S23. ECD spectra of (**11b**)$_2$ in tetrachloroethane and chloroform (top), temperature-dependent ECD and UV spectra of (**11b**)$_2$ in tetrachloroethane (bottom).

$(11c)_2$

Yield 90 %

$[\alpha]_D^{22}$ – 9.3 ± 0.1 (c 0.005 gcm^{-3} in DMF)

^{1}H NMR (400 MHz, $CDCl_3$): δ 14.19 (s, 4H, e_5-*OH*), 9.95 (s, 4H, *g*), 9.12 (s, 4H, e_3-*OH*), 8.07 (s, 4H, *f*), 7.86 (s, 4H, *l*), 7.81 (s, 4H, q_2), 7.23-7.44 (m, 20H, *k* + s, 4H, *h*), 7.18 (s, 4H, e_1), 5.93 (s, 4H, q_1), 5.41-5.50 (m, 4H, *i*), 4.51 (t, 4H, *J* = 7.2 Hz, *d*), 4.21-4.30 (m, 4H, *m*), 2.92-3.14 (m, 8H, *j*), 2.09-2.19 (m, 4H, c_2), 1.94-2.02 (m, 4H, *o*), 1.78-1.86 (m, 4H, c_1), 1.45-1.55 (m, 8H, *n*), 1.31-1.42 (m, 4H, *b*), 0.98 (d, 24H, *J* = 6.5 Hz, *a*), 0.92 (d, 12H, *J* = 5.0 Hz, p_2), 0.88 (d, 12H, *J* = 4.6 Hz, p_1).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8 (*s*), 172.2 (*t*), 154.0 (*r*), 152.1, 151.1 (e_3, e_5), 138.2 (*f*), 136.2 (k_1), 129.5 (k_2), 128.7 (k_3), 127.1 (k_4), 125.1 (e_1), 124.0, 123.7 (e_2, e_6), 107.0 (e_4), 54.1 (*i*), 52.3 (*m*), 43.1 (*c*), 42.0 (*j*), 41.3 (*n*), 30.5 (*d*), 26.1 (*b*), 24.4 (*o*), 22.9 (p_2), 22.6 (*a*), 22.5 (p_1).

HR MS (ESI): m/z calc for $[C_{112}H_{146}N_{20}O_{20}]^{2-}$ 1045.5506, found 1045.5524 (|Δ| = 1.7 ppm)

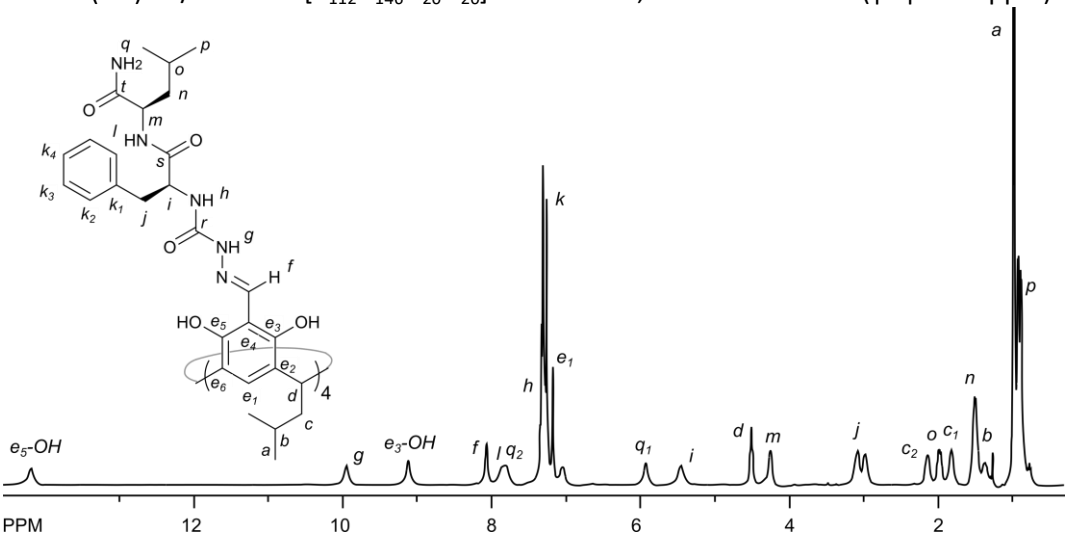


Figure S24. ^{1}H NMR spectrum of $(\mathbf{11c})_2$ ($CDCl_3$, 400 MHz).

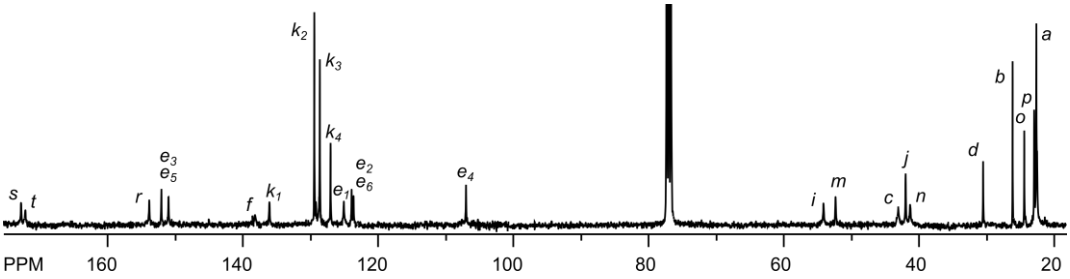


Figure S25. ^{13}C NMR spectrum of $(\mathbf{11c})_2$ ($CDCl_3$, 100 MHz).

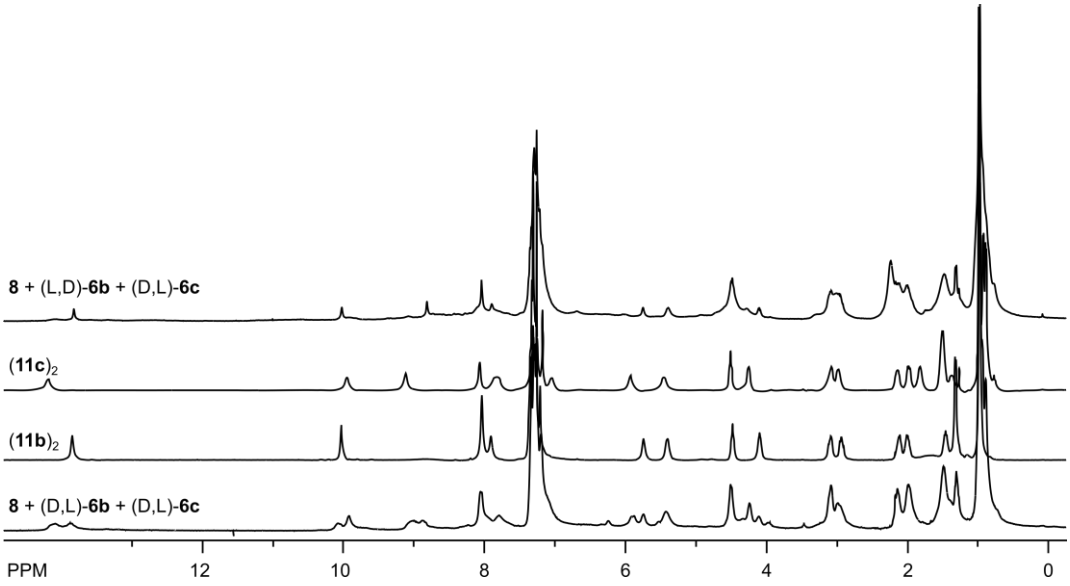


Figure S26. Self-sorting reaction of **8** with mixture of pseudoenantiomers **6b** and **6c** (^{1}H NMR, $CDCl_3$, 400 MHz).

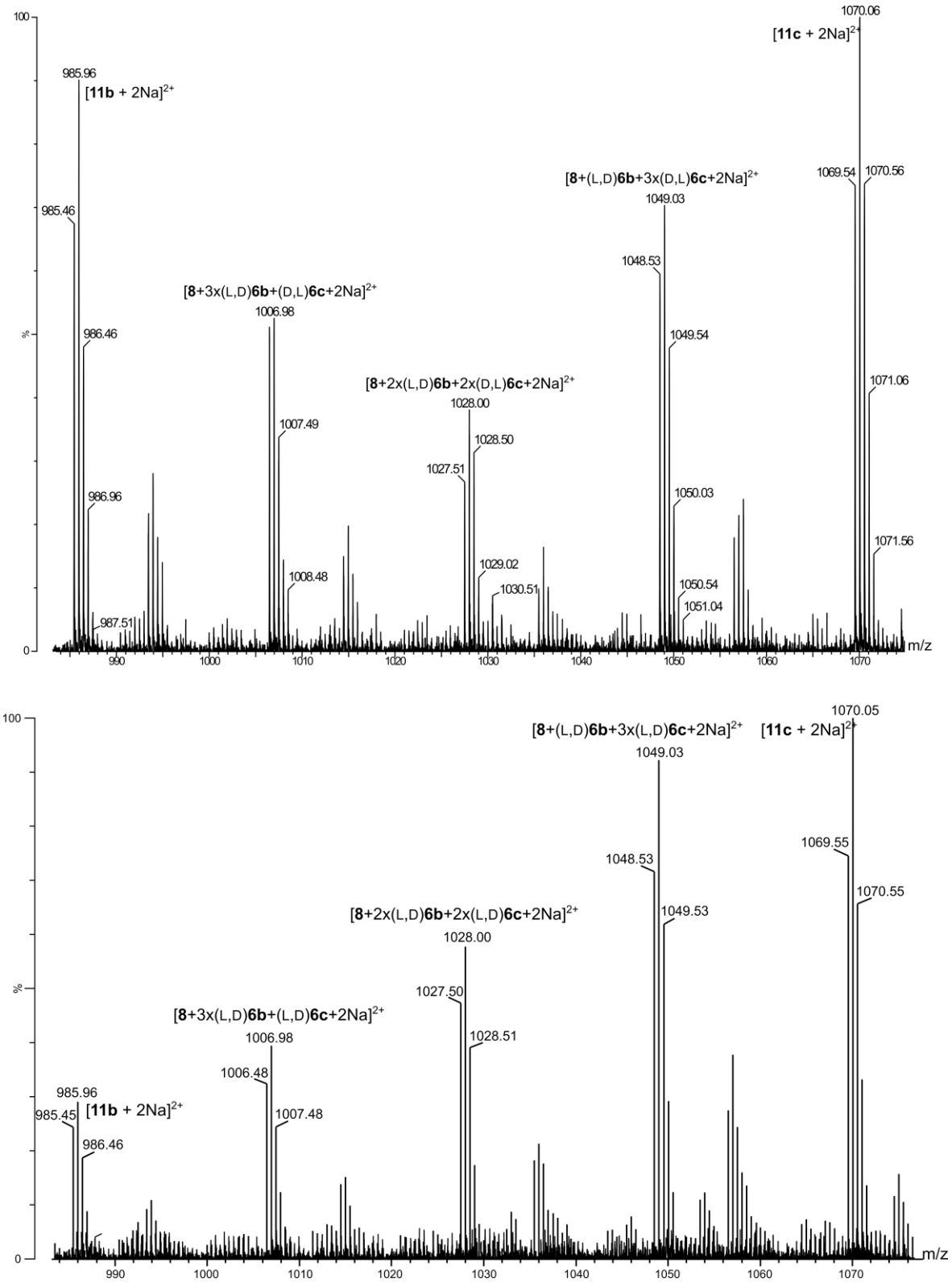


Figure S27. Self-sorting reaction of **8** with mixture of pseudoenantiomers (L,D)-**6b** and (D,L)-**6c** and comparison with reaction of **8** with mixture of (L,D)-**6b** and (L,D)-**6c** (ESI MS).

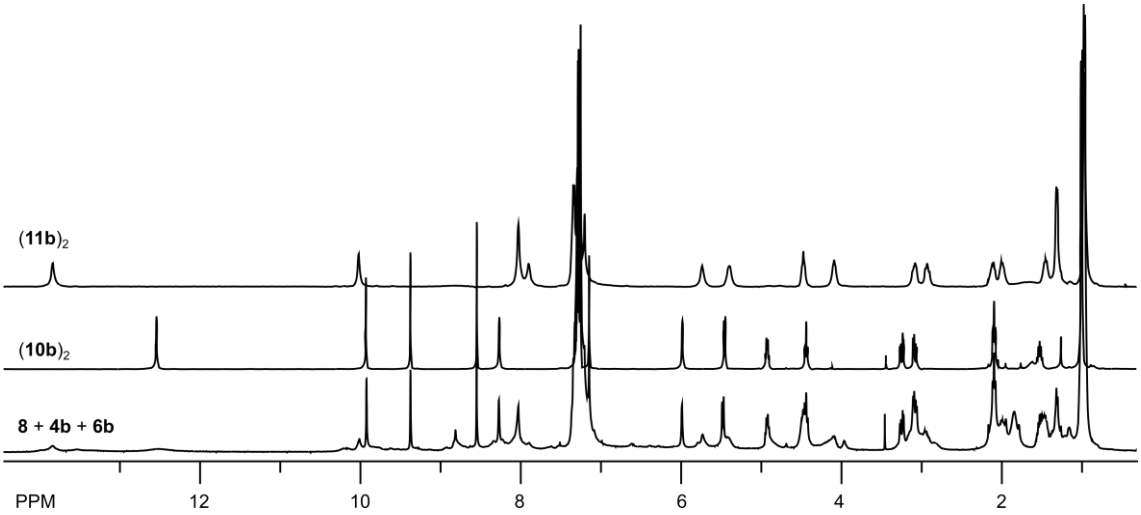


Figure S28. Self-sorting of peptides of different length (reaction of **8** with L-**4b** and (L,D)-**6b**) (^{1}H NMR spectra, $CDCl_3$, 400 MHz).

(D,L-11b)(L,L-11a)

Yield of self-sorting reaction 60 %

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.46 (br s, 4H, e_5-*OH*), 12.22 (br s, 4H, e_5-*OH*), 10.29 (s, 4H, *g'*), 9.94 (s, 4H, *g*), 9.39 (br s, 4H, e_3-*OH*), 9.38 (br s, 4H, e_3-*OH*), 8.51 (s, 4H, *f'*), 8.48 (s, 4H, o_2), 8.45 (s, 4H, *f*), 8.12 (s, 4H, o_2'), 7.14-7.35 (m, 20H, *k* + m, 20H, *k'* + d, 4H, *l'* + s, 4H, e_1), 7.13 (s, 4H, e_1'), 6.96 (d, 4H, *J* = 7.0 Hz, *l*), 6.47 (d, 4H, *J* = 5.9 Hz, *h*), 5.97 (d, 4H, *J* = 7.5 Hz, *h'*), 5.82 (s, 4H, o_1), 5.76 (s, 4H, o_1'), 5.19-5.22 (m, 4H, *i*), 4.78-4.90 (m, 12H, *m'* + *i'* + *m*), 4.48 (t, 4H, J = 8.0 Hz, d), 4.40 (t, 4H, J = 7.9 Hz, d'), 3.20 (dd, 4H, J_1 = 6.4 Hz, J_2 = 14.2 Hz, j_1), 3.00-3.12 (m, 12H, j_1' + j_2' + j_2), 2.02-2.17 (m, 16H, *c* + *c'*), 1.45-1.59 (m, 8H, *b* + *b'*), 1.34 (d, 12H, *J* = 6.7 Hz, *n*), 1.03 (d, 12H, *J* = 6.6 Hz, a_1), 1.01 (d, 12H, *J* = 6.6 Hz, a_2), 0.98 (d, 12H, *J* = 6.5 Hz, a_1'), 0.97 (d, 12H, *J* = 6.5 Hz, a_2'), 0.62 (d, 12H, *J* = 6.8 Hz, *n'*).

^{13}C NMR (150 MHz, $CDCl_3$): δ 176.1 (*s'*), 175.6 (*s*), 170.4 (*r'*), 170.2 (*r*), 154.3 (e_5'), 153.8 (e_5), 151.27 (*p*), 151.21 (*p'*), 151.0 (e_3 + e_3'), 143.3 (*f*), 142.4 (*f'*), 136.3 (k_1'), 136.1 (k_1), 130.1 (k_2), 129.7 (k_2'), 128.24, 128.23 (k_3 + k_3'), 126.9, 126.8 (k_4 + k_4'), 125.1 (e_1), 125.0 (e_1'), 124.4, 123.9, 123.8, 123.5 (e_2 + e_2' + e_6 + e_6'), 107.4 (e_4), 107.0 (e_4'), 53.9 (*i'*), 52.9 (*i*), 48.9 (*m*), 47.6 (*m'*), 41.5 (*j'*), 41.3, 41.2 (*c* + *c'*), 39.8 (*j*), 30.7 (*d*), 30.6 (*d'*), 26.1, 26.0 (*b* + *b'*), 22.76 (a_1), 22.71 (a_2), 22.67 (a_1'), 22.64 (a_2'), 21.0 (*n*), 19.2 (*n'*).

Diffusion coefficient obtained by DOSY 3.25 × 10^{-10} m^2s^{-1} in chloroform.

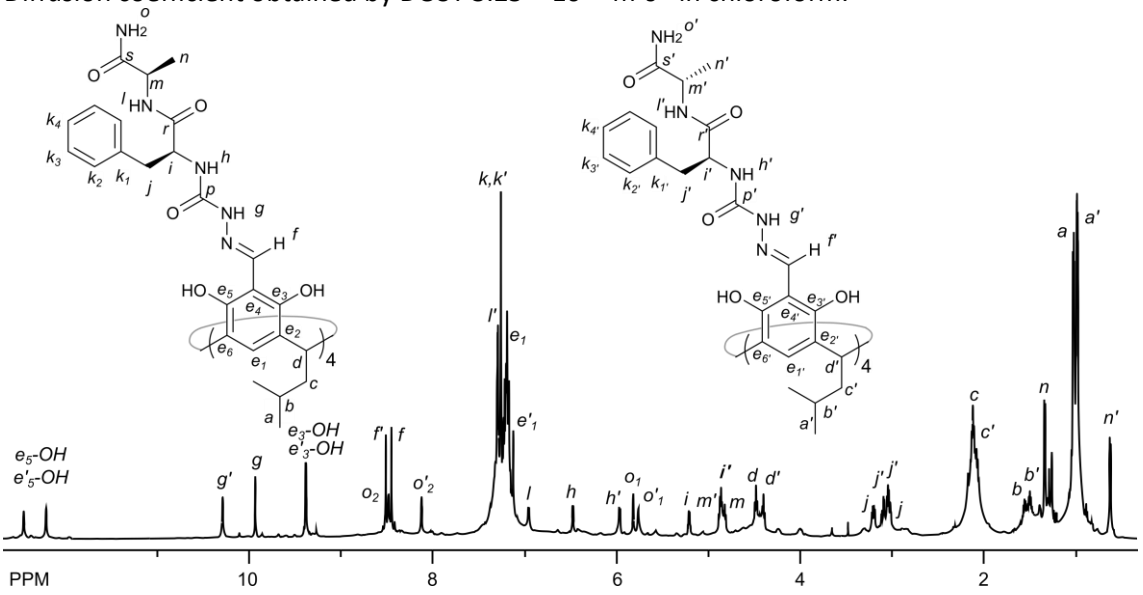


Figure S29. ^{1}H NMR spectrum of (D,L-**11b**)(L,L-**11a**) ($CDCl_3$, 600 MHz).

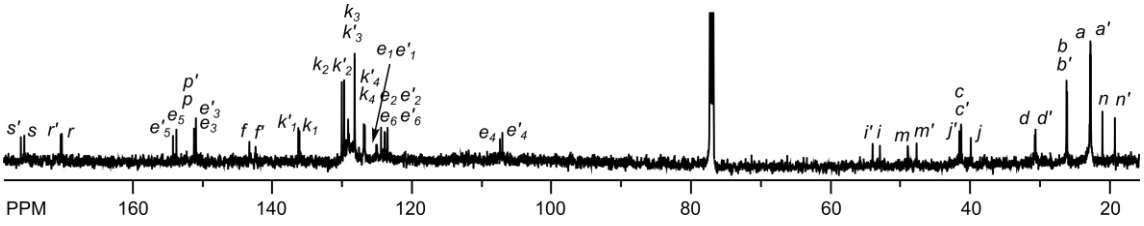


Figure S30. ^{13}C NMR spectrum of (D,L-**11b**)(L,L-**11a**) ($CDCl_3$, 150 MHz).

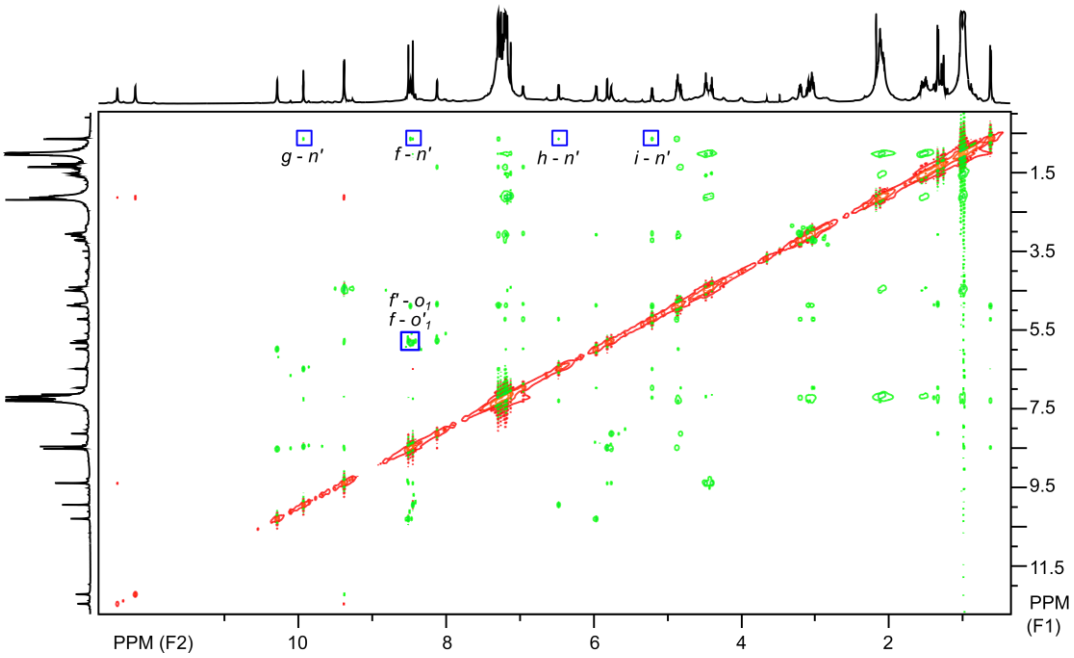


Figure S31. ROESY spectrum of (D,L-**11b**)(L,L-**11a**) ($CDCl_3$, 600 MHz, most indicative signals in frames).

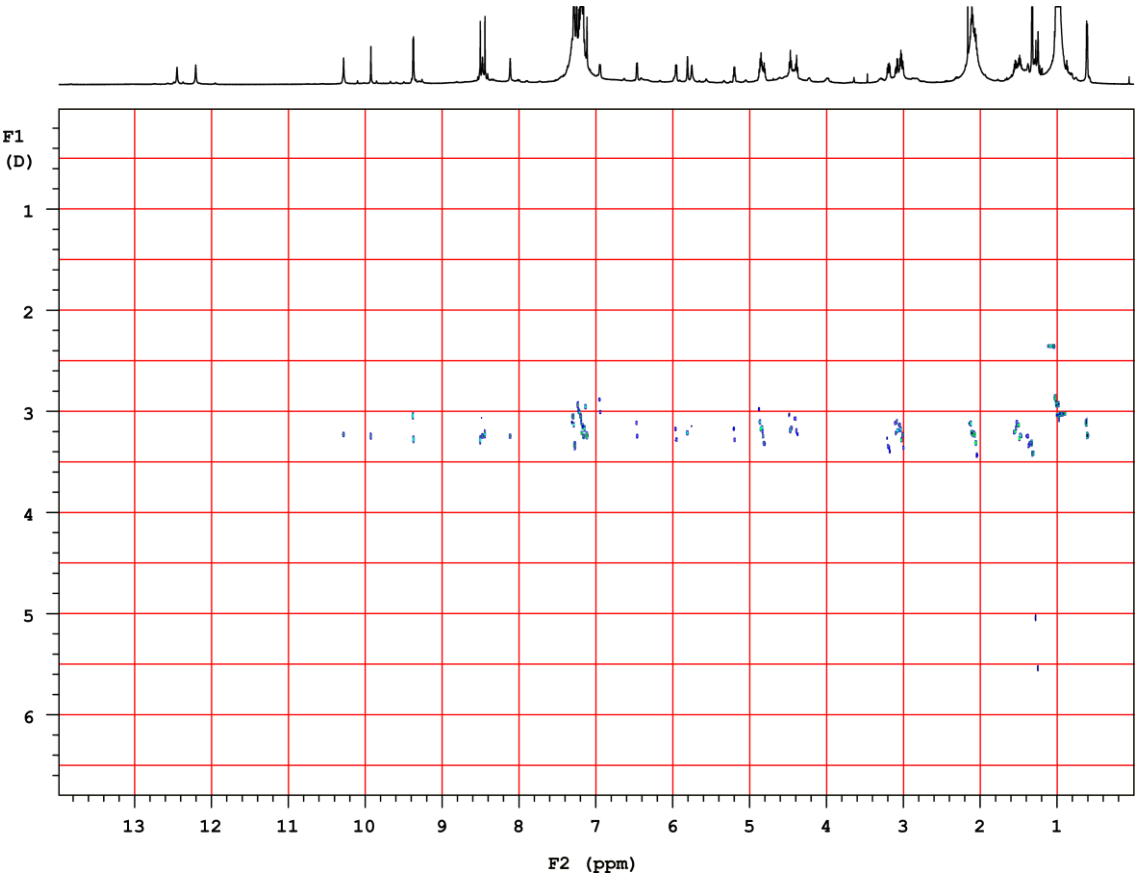


Figure S32. DOSY spectrum of (D,L-**11b**)(L,L-**11a**) ($CDCl_3$, 600 MHz).

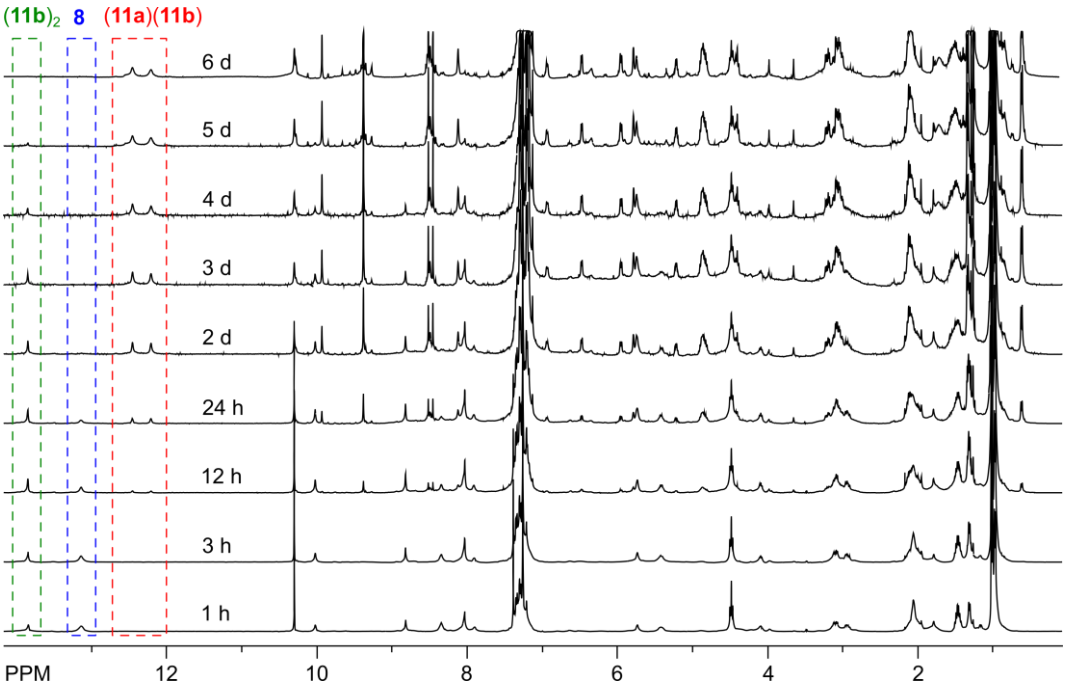


Figure S33. Self-sorting of peptides in reaction of **8** with (L,L)-**11a** and (D,L)-**11b** (^{1}H NMR spectra, $CDCl_3$, 400 MHz).

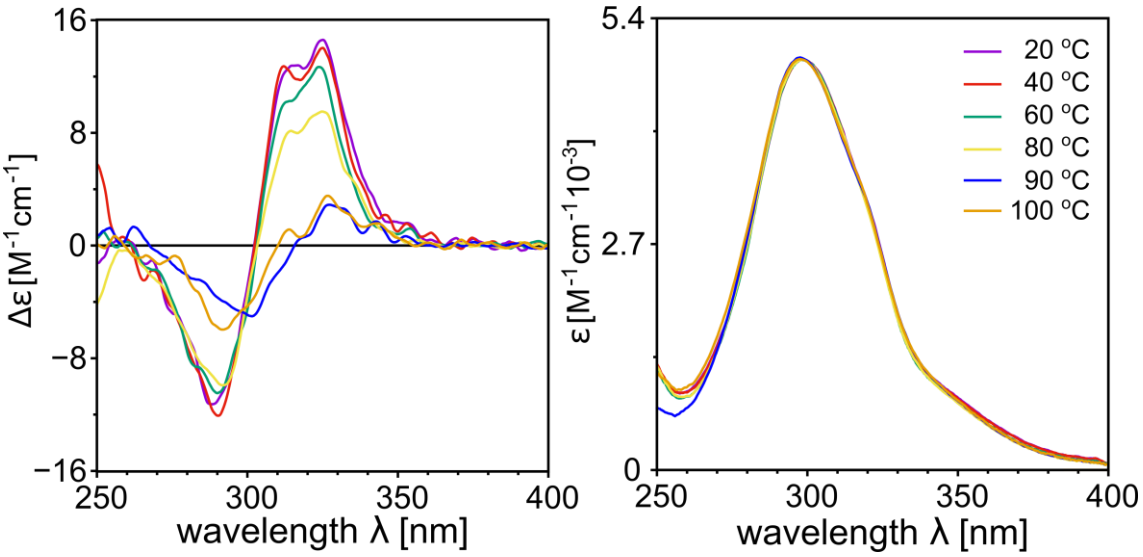


Figure S34. Temperature-dependent ECD and UV spectra of (D,L-**11b**)(L,L-**11a**) in tetrachloroethane.

$(12a)_2$

Yield 68 %

$[\alpha]_D^{22}$ – 63.8 ± 0.1 (c 0.009 gcm^{-3} in DMF)

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.46 (s, 4H, e_5-*OH*), 9.91 (s, 4H, *g*), 9.36 (s, 4H, e_3-*OH*), 8.51 (s, 4H, s_2), 8.44 (s, 4H, *f*), 7.21-7.33 (m, 20H, *k*, + s, 4H, *l*), 7.16 (s, 4H, e_1), 7.01 (d, 4H, *J* = 7.8 Hz, *o*), 6.48 (s, 4H, *J* = 4.6 Hz, *h*), 5.82 (s, 4H, s_1), 5.18-5.22 (m, 4H, *i*), 4.80-4.86 (m, 4H, *p*), 4.64-4.69 (m, 4H, *m*), 4.47 (t, 4H, *J* = 7.7 Hz, *d*), 3.19 (d, 8H, *J* = 4.3 Hz, *j*), 2.11 (dd, 8H, J_1 = 6.3 Hz, J_2 = 7.7 Hz, *c*), 1.51-1.57 (m, 4H, b), 1.41 (d, 12H, *J* = 6.3 Hz, *n*), 1.011 (d, 12H, *J* = 6.2 Hz, a_1), 1.008 (d, 12H, *J* = 6.1 Hz, a_2), 0.57 (d, 12H, *J* = 5.9 Hz, *r*).

^{13}C NMR (150 MHz, $CDCl_3$): δ 175.9 (*w*), 170.9 (*v*), 170.3 (*u*), 153.9 (*t*), 151.3, 151.2 (e_3 and e_5), 143.3 (*f*), 136.3 (k_1), 130.1 (k_2), 128.1 (k_3), 126.9 (k_4), 125.0 (e_1), 124.4, 123.9 (e_2 and e_6), 107.3 (e_4), 53.2 (*i*), 49.4 (*m*), 47.5 (*p*), 41.2 (*c*), 40.3 (*j*), 30.6 (*d*), 26.1 (*b*), 22.7 (a), 20.6 (*n*), 19.4 (*r*).

HR MS (ESI): m/z calc for $[C_{112}H_{142}N_{24}O_{24}]^{2-}$ 1103.5310, found 1103.5303 (|Δ| = 0.5 ppm)

Diffusion coefficient obtained by DOSY 3.0 × 10^{-10} m^{2}s^{-1} in chloroform.

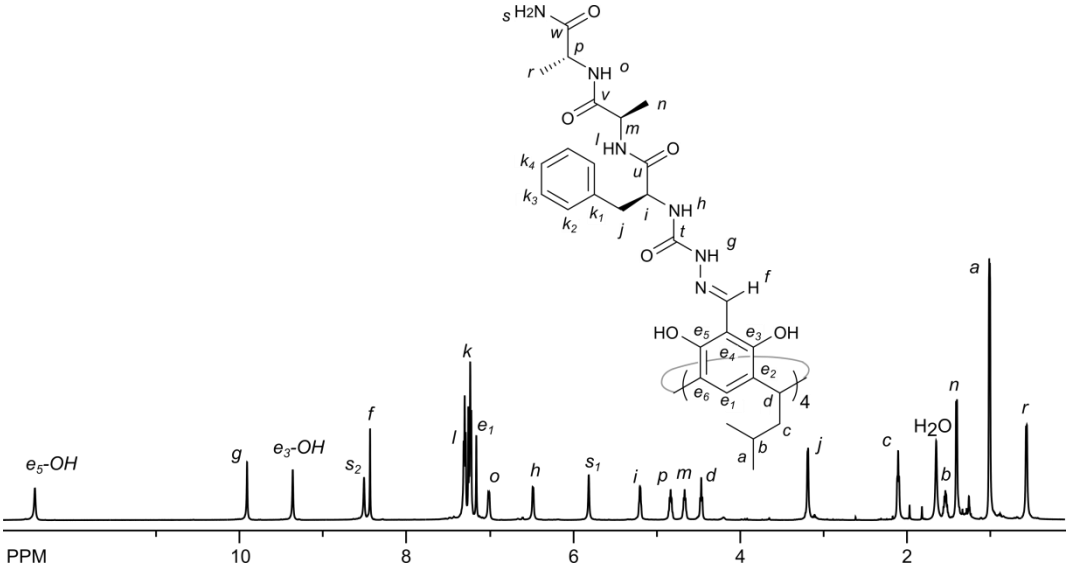


Figure S35. ^{1}H NMR spectrum of (**12a**)$_2$ ($CDCl_3$, 600 MHz).

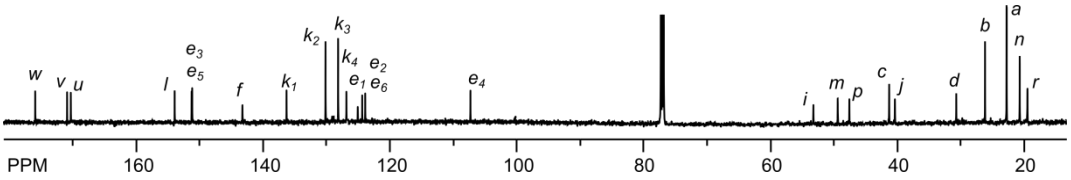


Figure S36. ^{13}C NMR spectrum of (**12a**)$_2$ ($CDCl_3$, 150 MHz).

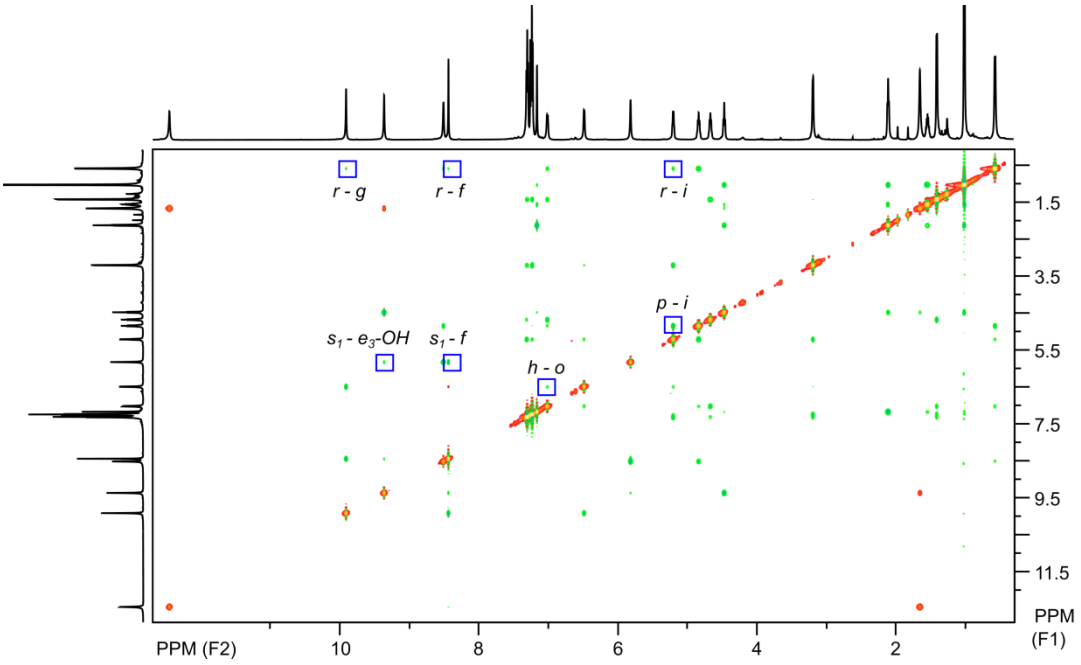


Figure S37. ROESY spectrum of (**12a**)$_2$ ($CDCl_3$, 600 MHz, most indicative signals in frames).

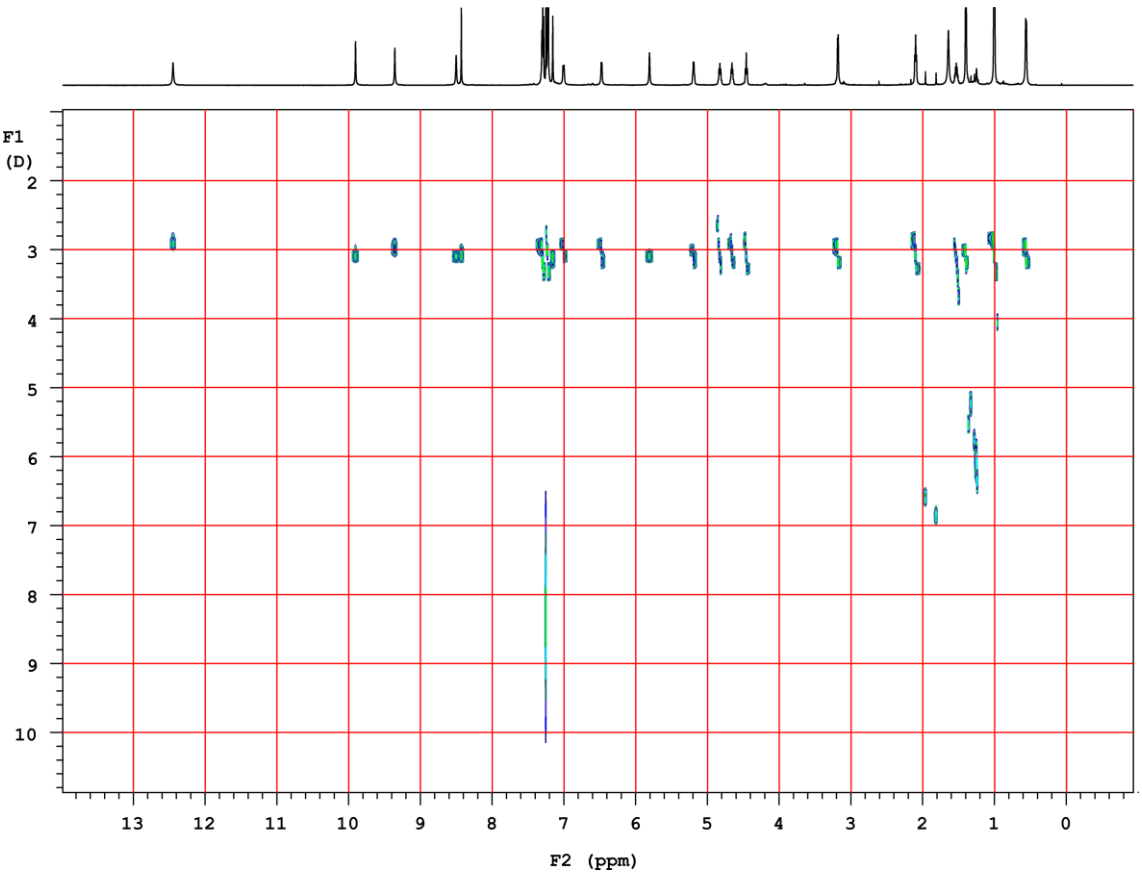


Figure S38. DOSY spectrum of (**12a**)$_2$ ($CDCl_3$, 600 MHz).

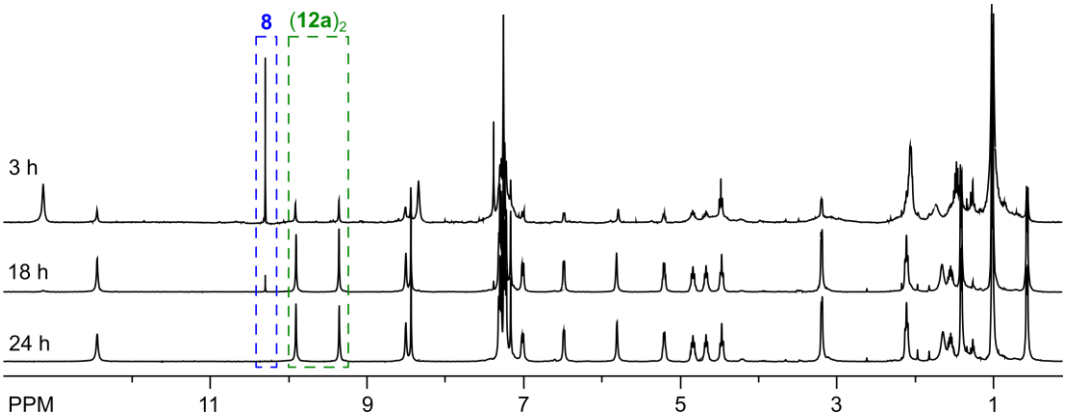


Figure S39. Reaction kinetics of **8** with L-**7a** ($CDCl_3$, 400 MHz).

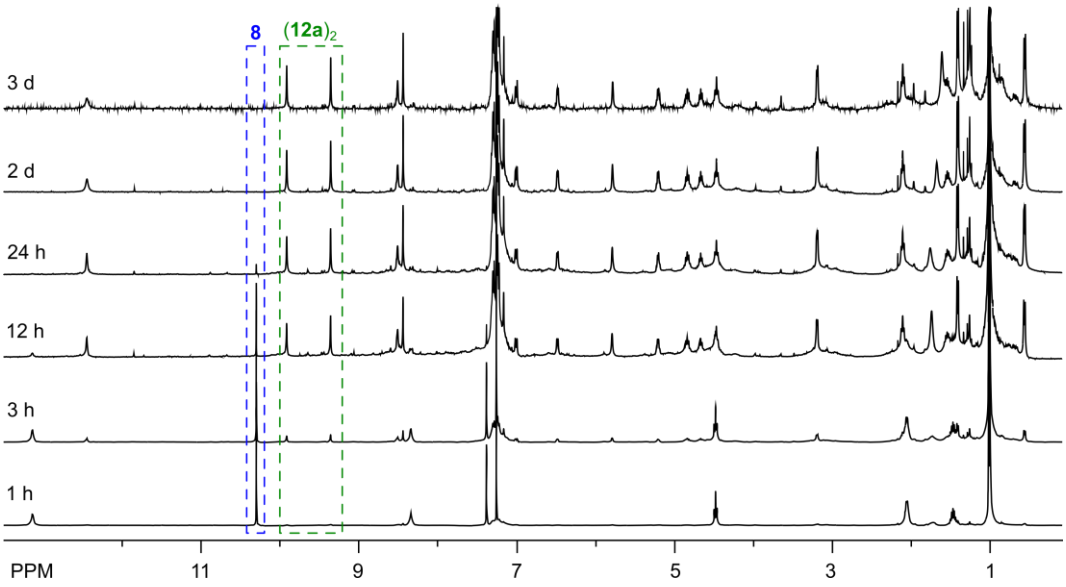


Figure S40. Chiral self-sorting of peptides in reaction of **8** with *rac*-**7a** (^{1}H NMR spectra, $CDCl_3$, 400 MHz).

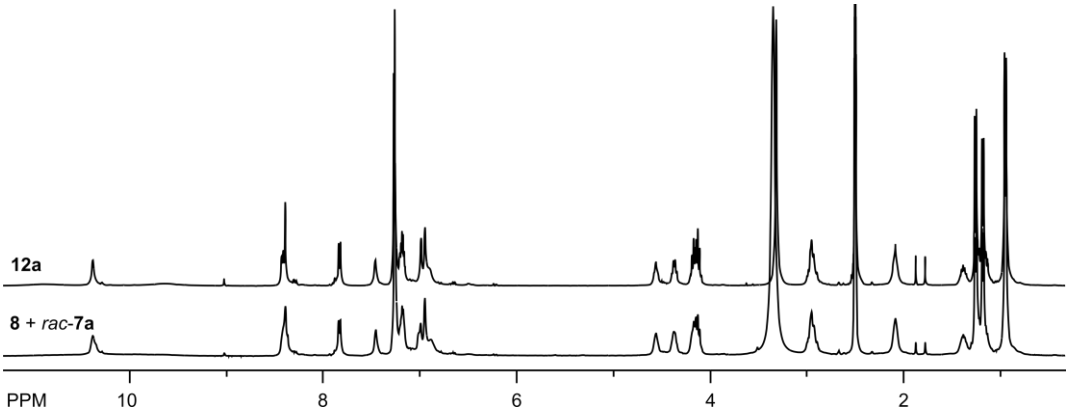


Figure S41. Chiral self-sorting of peptides in reaction of **8** with *rac*-**7a** (reaction in chloroform, 2 days, ^{1}H NMR spectra, DMSO-d_6, 400 MHz).

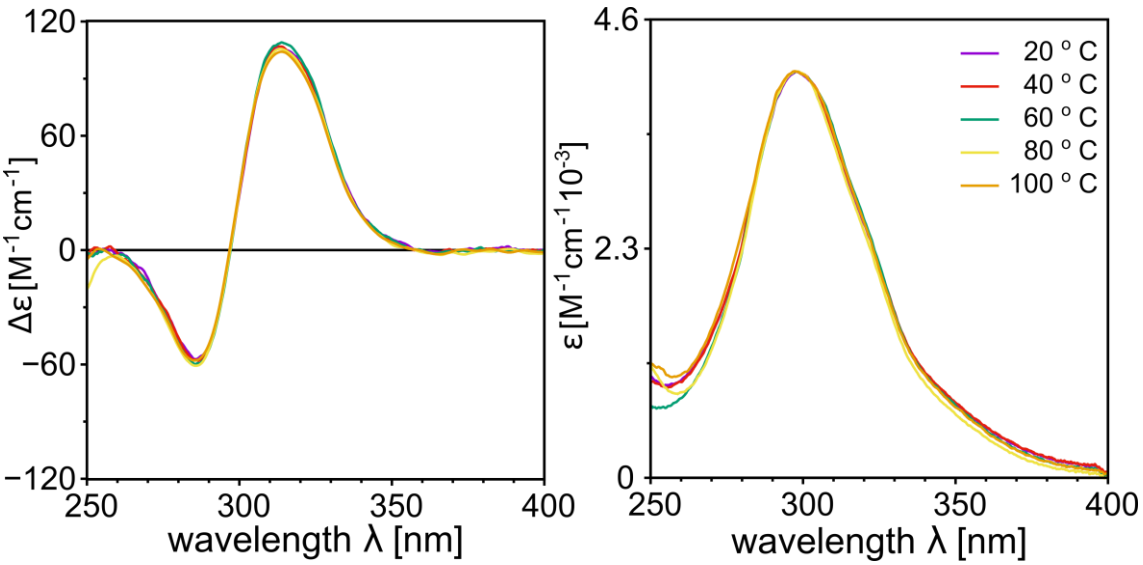


Figure S42. Temperature-dependent ECD and UV spectra of (**12a**)$_2$ in tetrachloroethane.

12b

Yield 66 % (precipitate from reaction in methanol)

$[\alpha]_D^{22}$ – 49.9 ± 0.7 (c 0.009 gcm^{-3} in DMF)

^{1}H NMR (500 MHz, DMSO-d_6): δ 11.16 (br s, 4H), 10.46 (s, 4H), 9.31 (br s, 4H), 8.51 (d, 4H, *J* = 5.1 Hz), 8.42 (s, 4H), 7.85 (d, 4H, *J* = 8.3 Hz), 7.49 (s, 4H), 7.12-7.30 (m, 20H + m, 20H + s, 4H), 7.10 (s, 4H), 7.04 (s, 4H), 4.54 (t, 4H, J = 6.1 Hz), 4.36-4.41 (m, 4H), 4.28-4.33 (m, 4H), 4.03-4.09 (m, 4H), 3.05-3.11 (m, 4H), 2.88-2.97 (m, 4H + m, 8H), 2.04-2.14 (m, 8H), 1.32-1.40 (m, 4H), 1.06 (d, 12H, *J* = 7.1 Hz), 0.93 (d, 24H, *J* = 6.3 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ 173.1, 172.5, 171.9, 154.5, 151.1, 150.9, 141.4, 138.2, 137.6, 129.3, 129.0, 128.14, 128.07, 127.0, 126.4, 126.2, 123.9, 123.7, 106.8, 55.3, 54.2, 49.0, 42.3, 37.3, 36.9, 30.6, 25.9, 22.7, 22.6, 17.4.

HR MS (ESI): m/z calc for $[C_{136}H_{158}N_{24}O_{24}]^{2-}$ 1255.5935, found 1255.5973 (|Δ| = 3.0 ppm)

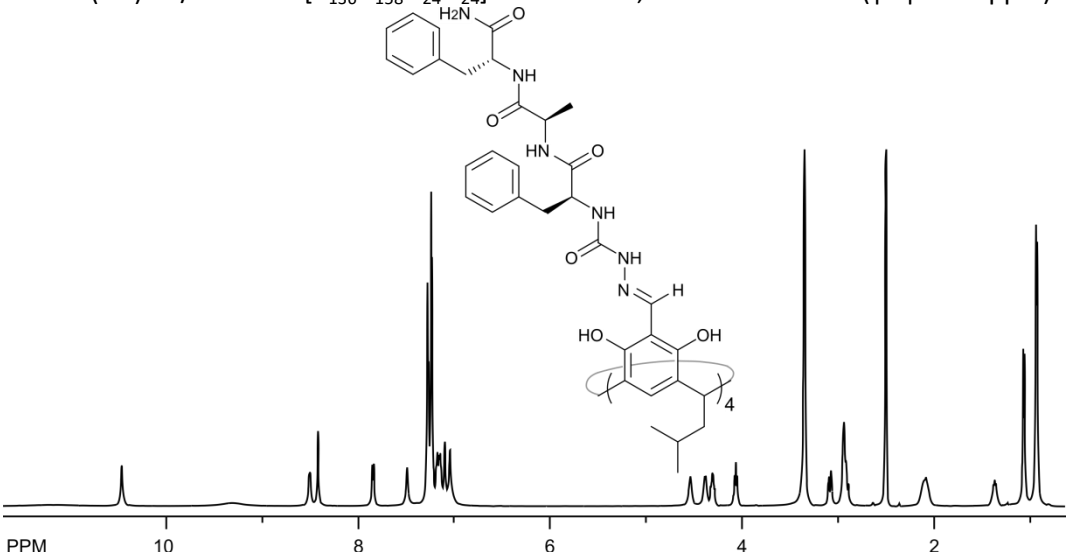


Figure S43. ^{1}H NMR spectrum of **12b** (DMSO-d_6, 500 MHz).

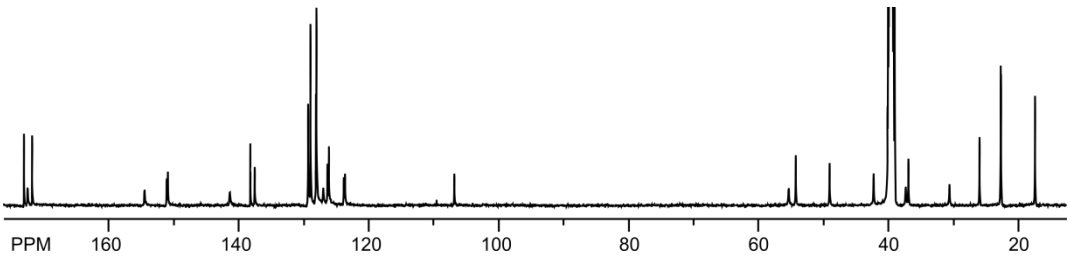


Figure S44. ^{13}C NMR spectrum of **12b** (DMSO-d_6, 125 MHz).

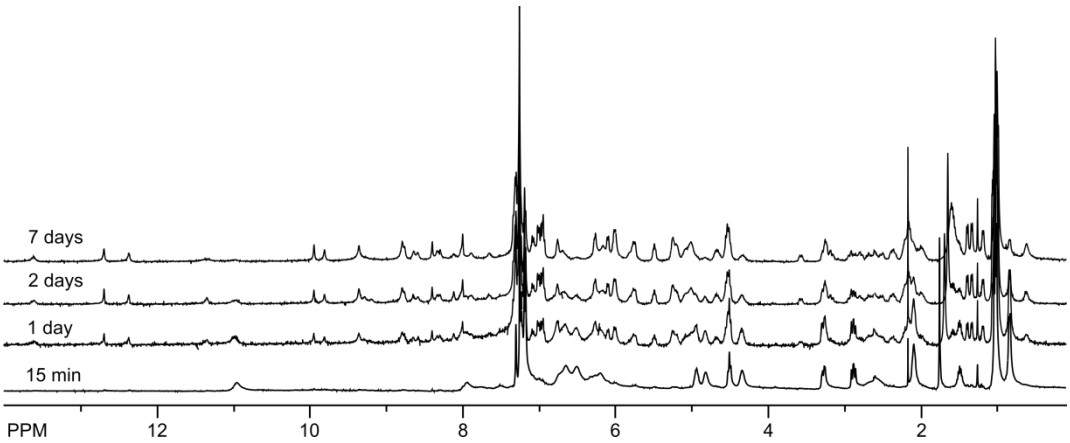


Figure S45. 1H NMR spectra of **12b** precipitate from methanol after dissolution in chloroform ($CDCl_3$, 400 MHz).

12c (two sets of signals)
Yield 55 %
$[\alpha]_D^{22}$ – 44.3 ± 0.2 (c 0.01 gcm^{-3} in DMF)
^{1}H NMR (600 MHz, $CDCl_3$): δ 12.25 (s, 4H, e_5-*OH*), 9.88 (s, 4H, *g*), 8.71 (s, 4H, e_3-*OH*), 8.47 (s, 4H, *f*), 8.41 (s, 4H, t_2),8.06 (d, 4H, *J* = 9.0 Hz, *o*), 7.67 (d, 4H, *J* = 8.6 Hz, *l*), 6.86-7.39 (m, 40H, *k* + *s*), 7.16 (s, 4H, e_1), 5.83 (br d, 4H, *h*), 5.79 (s, 4H, t_1), 5.01-5.07 (m, 4H, *i*), 4.51-4.58 (m, 8H, *p* + *m*), 4.33-4.36 (m, 4H, *d*), 2.88-2.96 (m, 8H, r_1 + j_1), 2.83 (dd, 4H, J_1 = 6.7 Hz, J_2 = 13.5 Hz, j_2), 2.73 (dd, 4H, J_1 = 9.6 Hz, J_2 = 13.4 Hz, r_2), 2.16-2.23 (m, 4H, c_1), 1.79-1.87 (m, 4H, c_2), 1.41-1.49 (m, 4H, *b*), 0.94-1.02 (m, 24H, *a*), 0.64 (d, 12H, *J* = 6.5 Hz, *n*).
^{13}C NMR (150 MHz, $CDCl_3$): δ 173.8 (*y*), 171.3 (*w*), 171.1 (*v*), 156.7 (*u*), 152.2, 151.4 (e_3 and e_5), 144.6 (*f*), 136.62 (k_1), 136.3 (s_1), 129.9 (k_2), 129.61 (s_2), (128.7, 128.3, 128.2, 128.0 (k_3, k_3', s_3 and s_3')), (127.0, 126.9, 126.7, 127.6 (k_4, k_4', s_4 and s_4')), 126.6 (e_2 or e_6), 123.4 (e_1), 122.9 (e_2 or e_6), 105.6 (e_4), 53.1 (*i*), 52.9 (*p*), 48.3 (*m*), 41.7 (*c*), 40.5 (*j*), 39.9 (*r*), 31.1 (*d*), 26.00 (*b*), 23.5 (*a*), 20.0 (*n*).

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.98 (s, 4H, e_5'-*OH*), 9.34 (s, 4H, *g'*), 8.65 (s, 4H, e_3'-*OH*), 8.63 (s, 4H, *f'*), 8.13 (s, 4H, t_2'), 7.52 (d, 4H, *J* = 9.0 Hz, *l'*), 6.86-7.39 (m, 40H, *k'* + *s'*), 6.81 (s, 4H, e_1'), 6.76 (d, 4H, *J* = 8.7 Hz, *o'*), 6.02 (s, 4H, t_1'), 5.59 (d, 4H, *J* = 9.0 Hz, *h'*), 5.33-5.38 (m, 4H, *p'*), 4.66-4.71 (m, 4H, *m'*), 4.37-4.31 (m, 4H, *i'*), 4.28-4.32 (m, 4H, *d'*), 3.35 (dd, 4H, J_1 = 9.7 Hz, J_2 = 13.2 Hz, j_1'), 3.20 (dd, 4H, J_1 4.1 = Hz, J_2 = 13.6 Hz, r_1'), 3.06 (dd, 4H, J_1 = 4.9 Hz, J_2 = 13.2 Hz, j_2'), 2.91-2.94 (m, 4H, r_2'), 2.16-2.23 (m, 4H, c_1'), 1.79-1.87 (m, 4H, c_2'), 1.41-1.49 (m, 4H, *b'*), 0.94-1.02 (m, 24H, *a'*), 0.83 (d, 12H, *J* = 6.8 Hz, *n'*).
^{13}C NMR (150 MHz, $CDCl_3$): δ 175.0 (*y'*), 172.0 (*w'*), 171.6 (*v'*), 154.9 (*u'*), 150.9, 150.7 (e_3' and e_5'), 145.5 (*f'*), 136.8 (k_1'), 136.58 (s_1'), 129.64 (s_2'), 129.5 (k_2'), (128.7, 128.3, 128.2, 128.0 (k_3, k_3', s_3 and s_3')), 127.1 (e_1'), (127.0, 126.9, 126.7, 127.6 (k_4, k_4', s_4 and s_4')), 123.9, 122.5 (e_2' and e_6'), 108.1 (e_4'), 56.7 (*l'*), 53.1 (*p'*), 47.0 (*m'*), 42.0 (*c'*), 40.2 (*r'*), 39.2 (*j'*), 30.3 (*d'*), 26.00 (*b'*), 22.1 (*a'*), 14.4 (*n'*).
HR MS (ESI): m/z calc for $[C_{136}H_{158}N_{24}O_{24}]^{2-}$ 1255.5935, found 1255.5962 (|Δ| = 2.2 ppm)
Diffusion coefficient obtained by DOSY 3.7 × 10^{-10} m^{2}s^{-1} in chloroform.

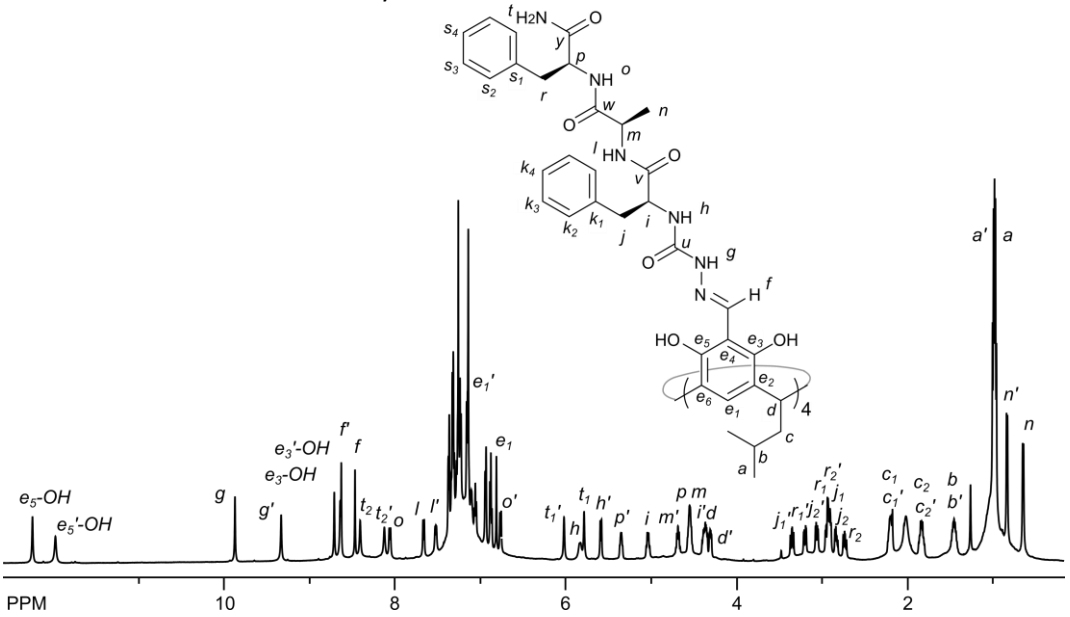


Figure S46. ^{1}H NMR spectrum of **12c** ($CDCl_3$, 600 MHz).

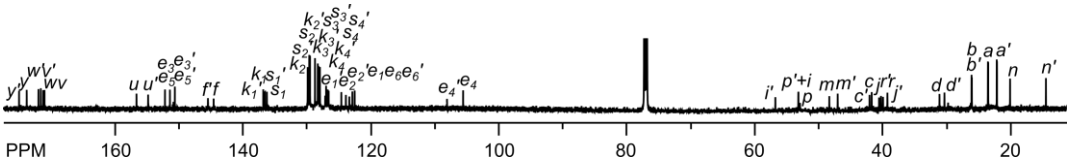


Figure S47. ^{13}C NMR spectrum of **12c** ($CDCl_3$, 150 MHz).

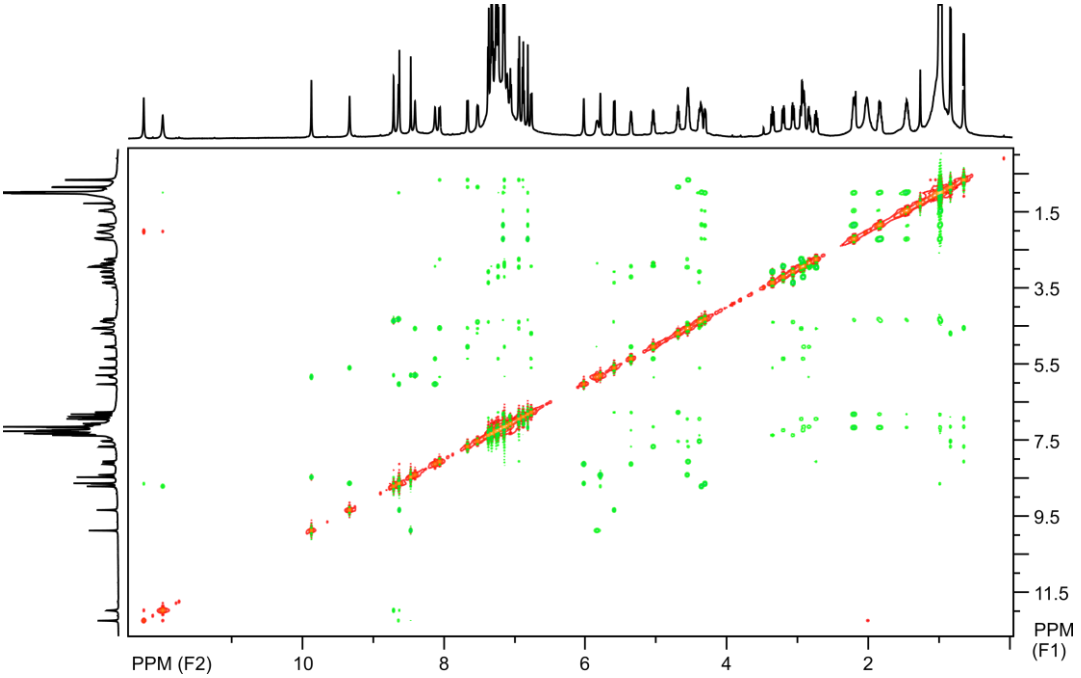


Figure S48. ROESY spectrum of **12c** ($CDCl_3$, 600 MHz).

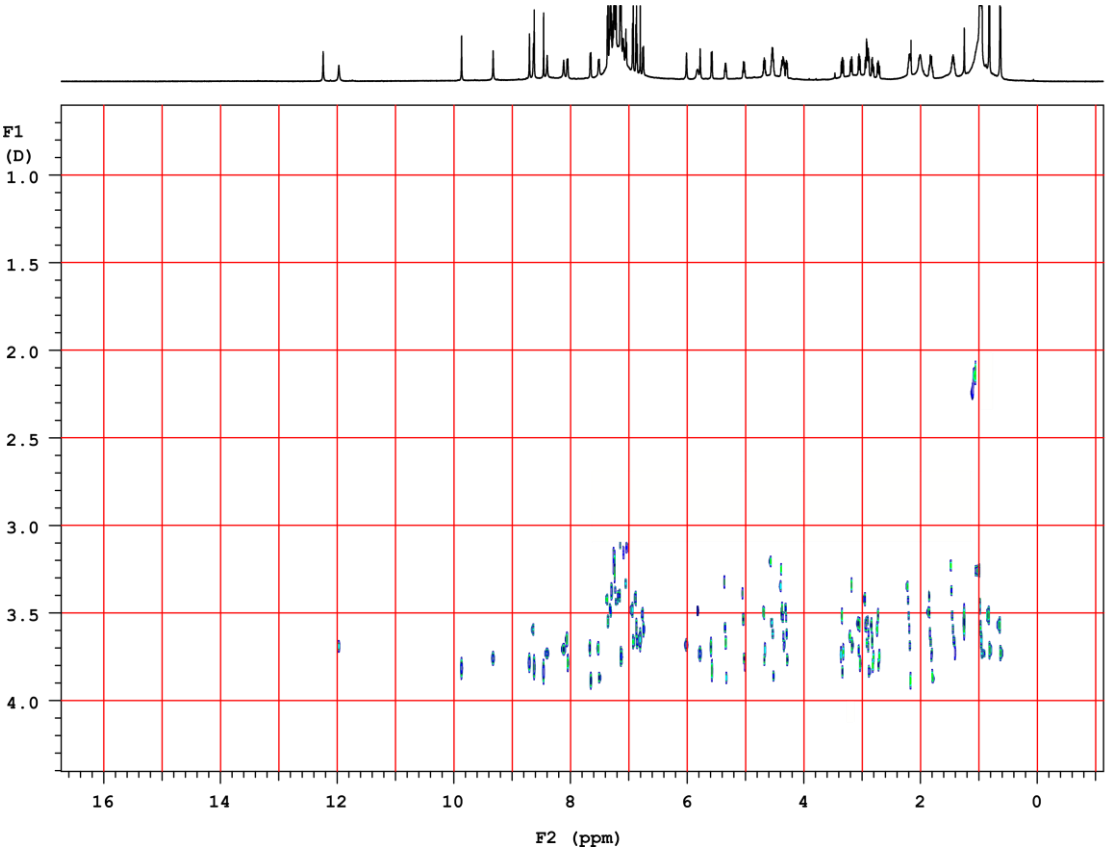


Figure S49. DOSY spectrum of **12c** ($CDCl_3$, 600 MHz).

12d

Yield 100 % (in DMSO)

$[\alpha]_D^{22}$ + 30.7 ± 0.1 (c 0.01 gcm^{-3} in DMF)

^{1}H NMR (500 MHz, DMSO-d_6): δ 10.35 (s, 8H), 8.37 (s, 4H), 8.27 (d, 4H, *J* = 7.4 Hz), 7.95 (d, 4H, *J* = 7.6 Hz), 7.45 (s, 4H), 7.15-7.28 (m, 20H + s, 4H + s, 4H), 6.97 (s, 4H), 6.85 (br d, 4 H), 4.57 (t, 4H, *J* = 7.7 Hz), 4.33-4.40 (m, 4H), 4.20-4.28 (m, 4H), 4.11-4.19 (m, 4H), 2.88-3.02 (m, 8H), 2.05-2.11 (m, 8H), 1.34-1.43 (m, 4H), 1.22 (d, 12H, *J* = 7.2 Hz), 1.15 (d, 12H, *J* = 7.0), 0.94 (d, 24H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, DMSO-d_6): δ 174.3, 171.7, 171.4, 159.5, 154.1, 151.2, 141.6, 137.6, 129.3, 128..2, 127.0, 126.4, 123.7 (2 C), 106.8, 55.3, 48.3 (2 C), 42.5, 37.7, 30.6, 26.0, 22.7, 18.0, 17.8.

HR MS (ESI): m/z calc for $[C_{112}H_{142}N_{24}O_{24}]^{2-}$ 1103.5309, found 1103.5331 (|Δ| = 2.0 ppm)

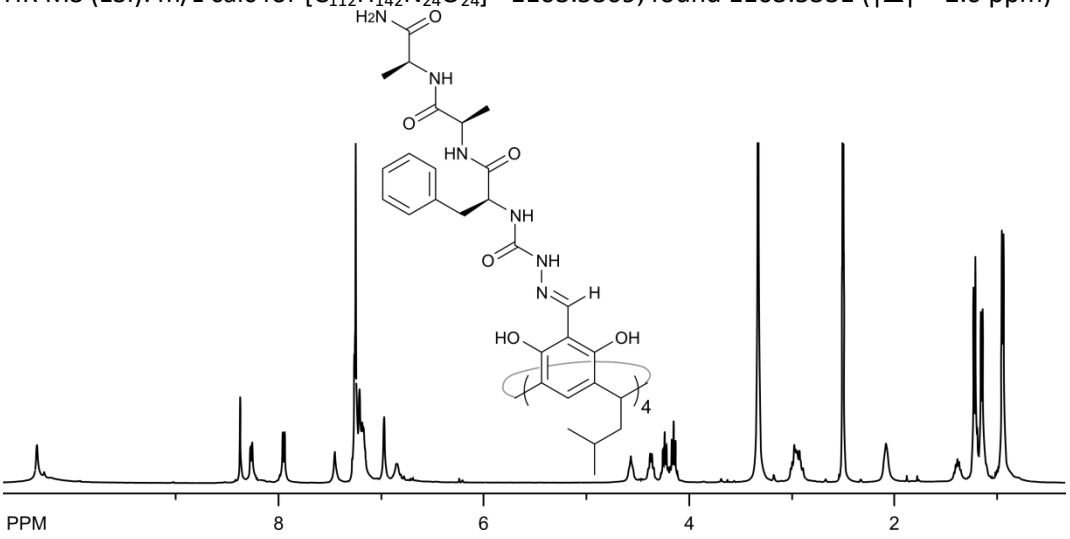


Figure S50. ^{1}H NMR spectrum of **12d** (DMSO-d_6, 500 MHz).

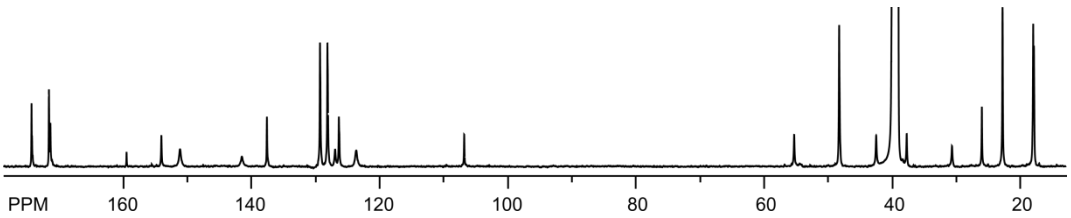


Figure S51. ^{13}C NMR spectrum of **12d** (DMSO-d_6, 125 MHz).

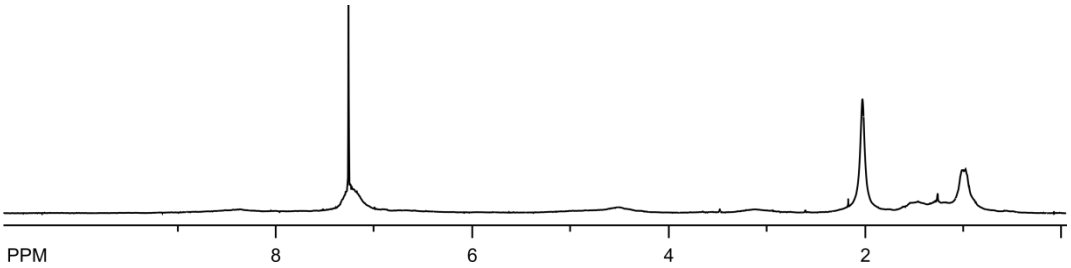


Figure S52. ^{1}H NMR spectrum of **12d** ($CDCl_3$, 400 MHz).

13

Yield 56 % (precipitate from chloroform)

$[\alpha]_D^{22}$ – 70.7 ± 0.1 (c 0.005 gcm^{-3} in DMF)

^{1}H NMR (400 MHz, DMSO-d$_6$): δ 10.51 (br s, 8H, *OH*), 10.11 (s, 4H, *g*), 8.39 (s, 4H, *f*), 7.43 (s, 4H, *h*), 7.20-7.39 (m, 20H, *k* + s, 1H, e_1), 4.81-4.90 (m, 4H, *i*), 4.53 (t, 4H, *J* = 7.7 Hz, *d*), 2.04-2.11 (m, 8H, *c*), 1.41 (d, 12H, *J* = 6.9 Hz, *j*), 1.34-1.40 (m, 4H, *b*), 0.93 (d, 24H, *J* = 6.5 Hz, *a*).

^{13}C NMR (100 MHz, DMSO-d$_6$): δ 153.7 (*l*), 151.0 (e_3 + e_5), 145.1 (k_1), 140.9 (*f*), 128.2 (k_2), 126.7 (e_1), 126.6 (k_4), 125.9 (k_3), 123.6 (e_2 + e_6), 106.9 (e_4), 48.8 (*i*), 42.3 (*c*), 40.2 (*j*), 30.7 (*d*), 25.9 (*b*), 22.7 (*a*).

HR MS (ESI): m/z calc for $[C_{84}H_{99}N_{12}O_{12}]^-$ 1467.7505, found 1467.7504 (|Δ| = 0.1 ppm)

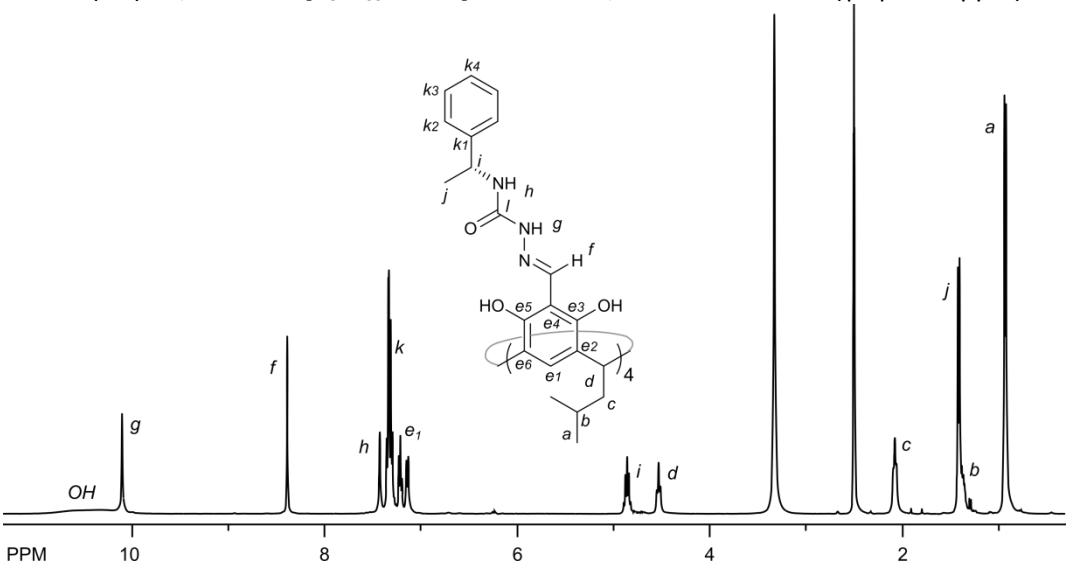


Figure S53. ^{1}H NMR spectrum of **13** (DMSO-d$_6$, 400 MHz).

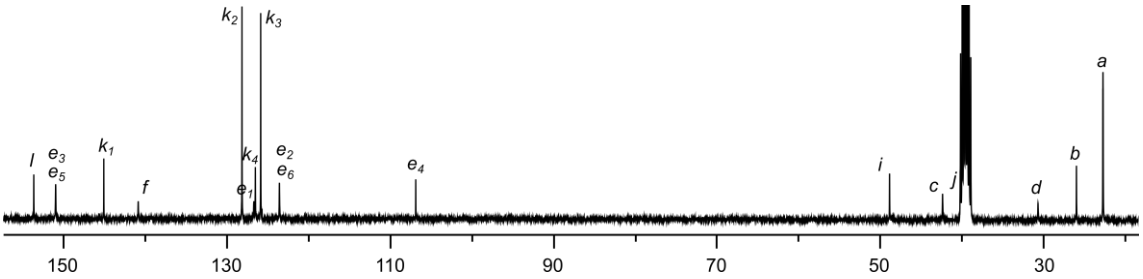


Figure S54. ^{13}C NMR spectrum of **13** (DMSO-d$_6$, 100 MHz).

Crystallographic data

CCDC 1883372 and CCDC 1883373 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data of (L-**10a**)$_2$ and (L,D-**11b**)$_2$.

Crystal data		
Moiety formula	(L-**10a**)$_4$(MeOH)$_2$($CHCl_3$)$_2$	(L,D-**11b**)$_2$(MeOH)($CHCl_3$)
Empirical formula	($C_{368}H_{448}N_{64}O_{64}$)($C_2H_8O_2$)($C_2Cl_6H_2$)	($C_{200}H_{248}N_{40}O_{40}$)($CH_4O$)($CCl_3H$)
Formula weight	7094.72	403.77
Temperature (K)	173	173
X-ray source	P13, Petra III, Hamburg	beamline 1911, MaxLab, Lund
Wavelength (Å)	0.68880	0.8000
Crystal system	triclinic	monoclinic
Space group	P-1	C2
Unit cell dimensions a/b/c (Å)	22.497(5) 31.279(6) 36.562(7)	36.060 35.480 22.490
Unit cell angles α/β/γ (°)	67.29(3) 79.62(3) 88.00(3)	90 101.5 90
Unit cell volume (Å^3)	23329(8)	28196.3
Z	4	4
Calculated density (g/cm^3)	1.009	0.943
Absorption coefficient (mm^{-1})	0.095	0.127
F(000)	7524	8496
θ range for data collection (°)	24.55 – 0.59	24.931 – 0.915
Index ranges	-26 < h <27 -34 < k < 37 0 < l < 44	-36 < h <36 -36 < k < 34 -23 < l < 23
Reflections collected	266161	91523
Independent reflections	78521 (R_{int} = 0.0578)	29386 (R_{int} = 0.0979)
Completeness to θ_{max}	0.915	0.878
Refinement statistics		
Final R indices [>2σ(I)]	0.0731	0.0986
R indices [all data]	0.0977	0.1194
Goodness-of-fit	1.128	1.139
Extinction coefficient	-	-
Largest diff. peak and hole (e Å^{-3})	0.81 / -0.42	0.39 / -0.35

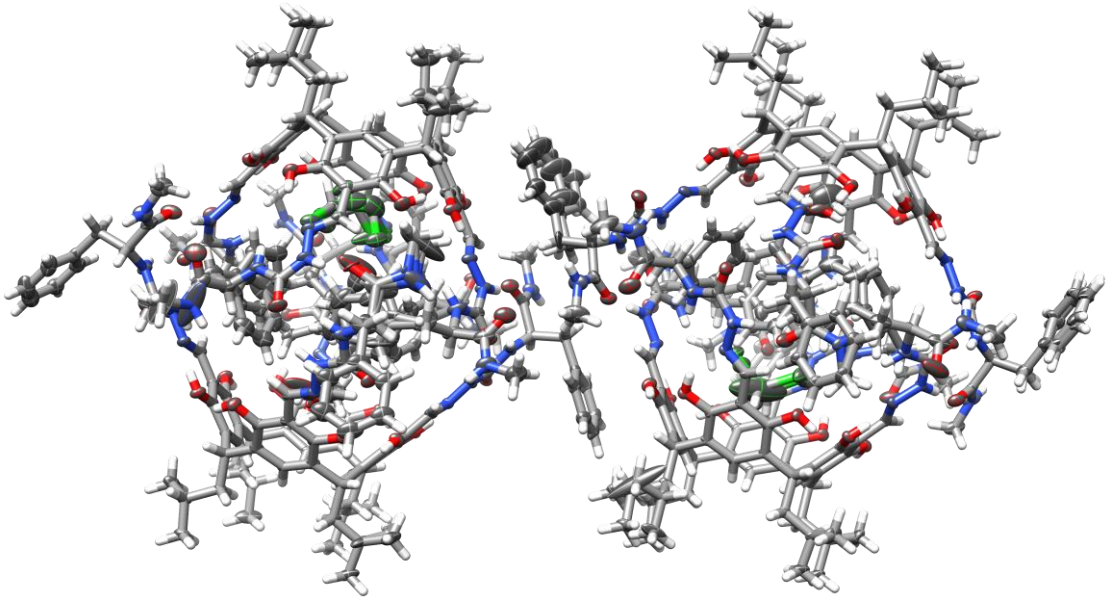


Figure S55. ORTEP representation of crystallographically independent part of (L-**10a**)$_2$ capsule. Thermal ellipsoids are depicted at 50% probability.

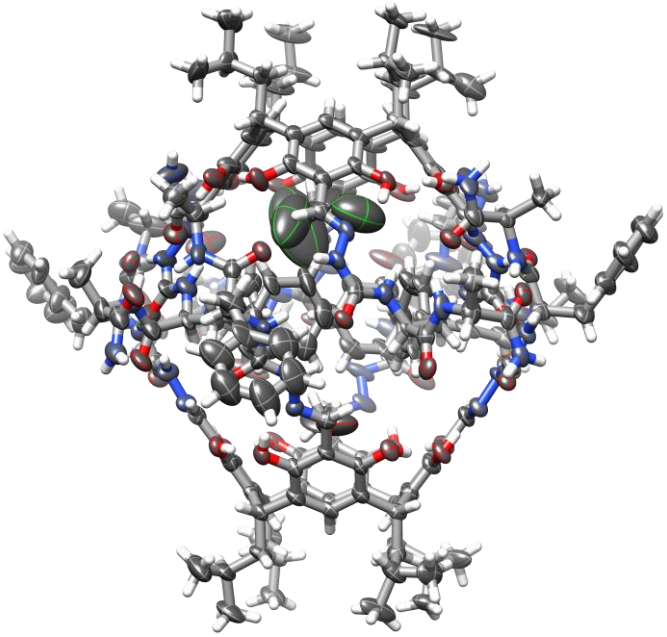


Figure S56. ORTEP representation of crystallographically independent part of (L,D-**11b**)$_2$ capsule. Thermal ellipsoids are depicted at 30% probability.

Details of crystal structure analyses and explanation of CHECKCIF alerts

Data collection and data quality:
The samples of capsules were crystallized by the diffusion method using chloroform/methanol mixture. Prior to the measurement crystals were transferred quickly from mother liquor to immersion oil and frozen to avoid solvent loss. Data were collected using synchrotron beamlines (P13, Petra III, Hamburg for (L-**10a**)$_2$, 1911, MaxLab, Lund for (L,D-**11b**)$_2$). The structures were solved using SHELXS[6] ((L-**10a**)$_2$) or by molecular replacement using the PHASER[7] module of the CCP4 suite[8] ((L,D-**11b**)$_2$). For all the crystals of peptidic capsules, crystal lattices contained substantial voids (intramolecular and intermolecular) that were filled with highly disordered solvent molecules. All the crystals were found to be weakly diffracting and as a result, reflections did not extend out as far in theta as what would normally be considered desirable for small molecules. This led to some level A alert being generated by the CHECKCIF program.

Refinement and treatment of disorder
All non-hydrogen atoms that were not disordered where refined anisotropically. Hydrogen atoms were positioned using geometrical restraints. In all cases procedures were applied in order to remove highly disordered solvent molecules present in intracapsular and intercapsular voids. Solvent masking procedure implemented in OLEX2 was used.[9]

Explanation of level A alerts for the crystal structure of (L-10a)$_2$

Alert level A

```
PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.915 Why?
```

The crystals were found to be weakly diffracting and as a result, reflections did not extend out as far in theta as what would normally be considered desirable for small molecules.

```
PLAT213_ALERT_2_A Atom N4B_18 has ADP max/min Ratio ..... 5.7 prolat
PLAT213_ALERT_2_A Atom C5B_18 has ADP max/min Ratio ..... 16.4 prolat
PLAT213_ALERT_2_A Atom C6C_13 has ADP max/min Ratio ..... 5.3 prolat
PLAT213_ALERT_2_A Atom C12B_2 has ADP max/min Ratio ..... 5.2 prolat
PLAT213_ALERT_2_A Atom C1A_22 has ADP max/min Ratio ..... 8.8 oblate
PLAT213_ALERT_2_A Atom C2A_22 has ADP max/min Ratio ..... 5.4 prolat
PLAT214_ALERT_2_A Atom C21C_26 (Anion/Solvent) ADP max/min Ratio 8.1 prolat
```

These atoms are disordered and could not be satisfactorily refined anisotropically.

```
PLAT413_ALERT_2_A Short Inter XH3 .. XHn H10_16 ..H1AA_26 . 1.88 Ang.
x,y,z = 1_555 Check
```

H1AA_26 is hydrogen in CH_3 group in methanol molecule, this group can rotate.

```
PLAT602_ALERT_2_A VERY LARGE Solvent Accessible VOID(S) in Structure ! Info
```

The above alert is caused by the use of the solvent masking procedure in the refinement of disordered solvent molecules.

Explanation of level A alerts for the crystal structure of (L,D-11b)$_2$

Alert level A

```
THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.5269
```

The above alert comes from weak diffraction of the crystals and subsequent poor quality of the data.

```
PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full value Low . 0.878 Why?
```

The crystals were found to be weakly diffracting and as a result, reflections did not extend out as far in theta as what would normally be considered desirable for small molecules.

```
PLAT213_ALERT_2_A Atom N65A has ADP max/min Ratio ..... 6.4 prolat
PLAT213_ALERT_2_A Atom C67B has ADP max/min Ratio ..... 5.2 oblate
```

These atoms are disordered and could not be satisfactorily refined anisotropically.

PLAT260_ALERT_2_A Large Average Ueq of Residue Including Cl2S 0.752 Check
PLAT260_ALERT_2_A Large Average Ueq of Residue Including O10S 0.324 Check

These alerts are generated by substantial thermal mobility of solvent molecules (as indicated by large thermal parameters), additional disorder is still possible.

PLAT413_ALERT_2_A Short Inter XH3 .. XHn H14C ..H19G . 1.86 Ang.
1-x,y,2-z = 2_657 Check

These atoms come from two methyl groups. The hydrogens were placed geometrically and therefore their real positions may vary by rotation.

PLAT430_ALERT_2_A Short Inter D...A Contact O64 ..O69B . 2.36 Ang.
-x,y,2-z = 2_557 Check

These atoms are disordered and could not be satisfactorily modelled.

Ab initio calculations

All calculations were performed within the density functional theory (DFT) approach using Gaussian 09 program suite.[10] Geometry was optimized with the B3LYP functional, employing the 6-31G+(d,p) basis set. Solvent effects were considered within the SCRF theory using the polarized continuum model (PCM) approach to model the interaction with the solvent. Excited electronic states were determined at the B3LYP/6-31G+(d,p) level by means of the time-dependent DFT (TD DFT) approach (100 excited states in each case). The ECD spectra were simulated by overlapping Gaussian functions for each transition where the width of the band at 1/e height is fixed at 0.2 eV and the resulting intensities of the combined spectra were scaled to the experimental values (using UV-VIS spectra as references). Presentation of molecular orbitals was performed by using the GaussView program.
Model compounds without any additional chromophores deriving from amino acids were used for theoretical calculations. Aliphatic chains at lower rim were shortened since their lengths have negligible influence on UV-VIS and ECD spectra.

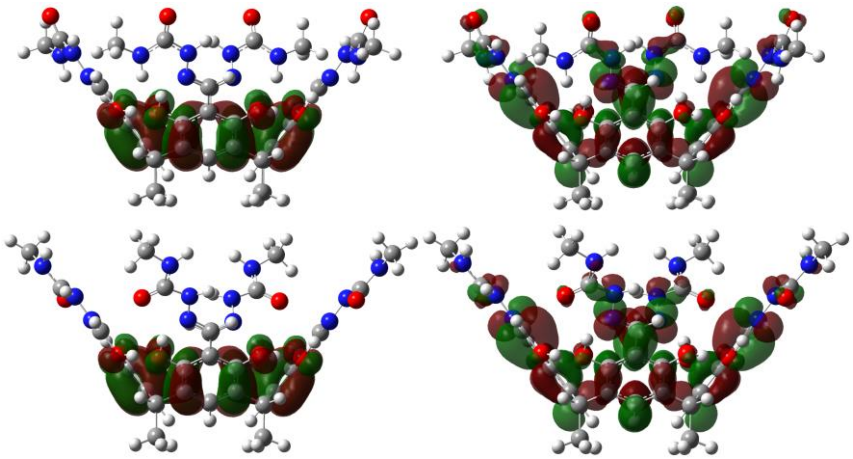


Figure S57. HOMO (left) and LUMO (right) orbitals of C_4 symmetrical AzaGlyNMe cavitands with *cis* (up) and *trans* (bottom) configuration.

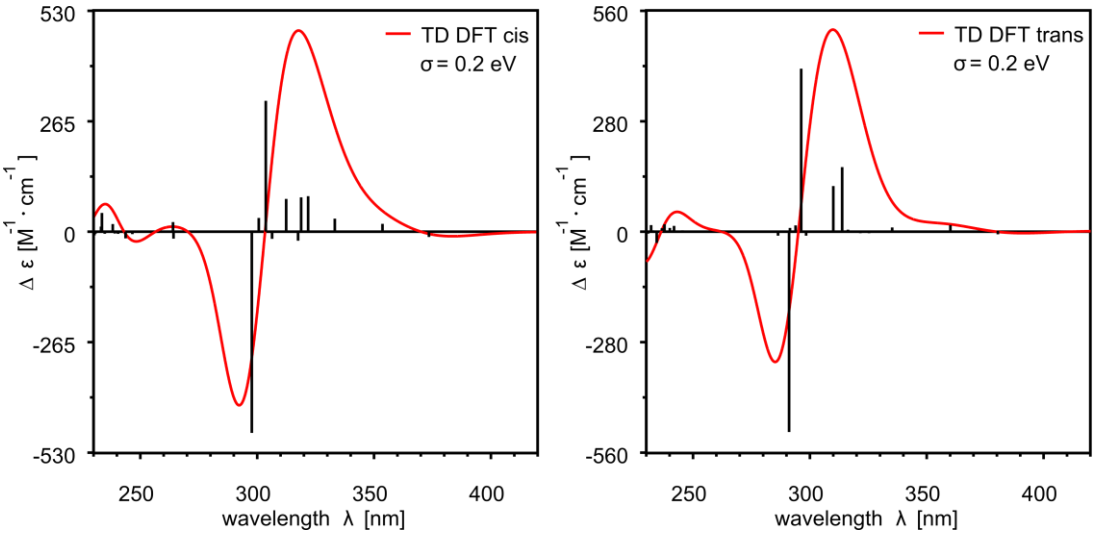


Figure S58. Calculated ECD spectra of C_4 symmetrical AzaGlyNMe cavitands with *cis* (left) and *trans* (right) configuration.

Atomic coordinates for calculated geometries

AzaGlyNMe cavitand *cis*
Total energy = -3267.96273939 a.u.

	x	y	z
O	-0.43378200	4.95724800	0.51778400
O	3.90470700	2.98758100	0.34382100
C	0.48752300	4.07601900	1.02486600

C	1.76598600	3.97442000	0.42963000
C	2.69108900	3.04138000	0.96211200
C	2.36492300	2.25693500	2.08202200
C	1.07615500	2.39584100	2.61185200
C	0.11499400	3.28052300	2.11443900
C	2.14875300	4.76019100	-0.73173400
N	1.38653100	5.68906000	-1.21842000
N	1.79923900	6.33884400	-2.34059000
C	1.12145800	7.41518700	-2.91411000
O	1.51751100	7.87330100	-3.98312000
C	3.38708700	1.29517600	2.70245300
C	3.35445200	1.30255800	4.24373700
O	4.95724800	0.43378200	0.51778400
O	2.98758100	-3.90470700	0.34382100
C	4.07601900	-0.48752300	1.02486600
C	3.97442000	-1.76598600	0.42963000
C	3.04138000	-2.69108900	0.96211200
C	2.25693500	-2.36492300	2.08202200
C	2.39584100	-1.07615500	2.61185200
C	3.28052300	-0.11499400	2.11443900
C	4.76019100	-2.14875300	-0.73173400
N	5.68906000	-1.38653100	-1.21842000
N	6.33884400	-1.79923900	-2.34059000
C	7.41518700	-1.12145800	-2.91411000
O	7.87330100	-1.51751100	-3.98312000
C	1.29517600	-3.38708700	2.70245300
C	1.30255800	-3.35445200	4.24373700
O	-4.95724800	-0.43378200	0.51778400
O	-2.98758100	3.90470700	0.34382100
C	-4.07601900	0.48752300	1.02486600
C	-3.97442000	1.76598600	0.42963000
C	-3.04138000	2.69108900	0.96211200
C	-2.25693500	2.36492300	2.08202200
C	-2.39584100	1.07615500	2.61185200
C	-3.28052300	0.11499400	2.11443900
C	-4.76019100	2.14875300	-0.73173400
N	-5.68906000	1.38653100	-1.21842000
N	-6.33884400	1.79923900	-2.34059000
C	-7.41518700	1.12145800	-2.91411000
O	-7.87330100	1.51751100	-3.98312000
C	-1.29517600	3.38708700	2.70245300
C	-1.30255800	3.35445200	4.24373700
O	0.43378200	-4.95724800	0.51778400
O	-3.90470700	-2.98758100	0.34382100
C	-0.48752300	-4.07601900	1.02486600
C	-1.76598600	-3.97442000	0.42963000
C	-2.69108900	-3.04138000	0.96211200
C	-2.36492300	-2.25693500	2.08202200
C	-1.07615500	-2.39584100	2.61185200
C	-0.11499400	-3.28052300	2.11443900
C	-2.14875300	-4.76019100	-0.73173400
N	-1.38653100	-5.68906000	-1.21842000
N	-1.79923900	-6.33884400	-2.34059000
C	-1.12145800	-7.41518700	-2.91411000
O	-1.51751100	-7.87330100	-3.98312000
C	-3.38708700	-1.29517600	2.70245300
C	-3.35445200	-1.30255800	4.24373700
H	0.81149600	1.78852300	3.47072400
H	3.11061300	4.52621500	-1.19122000
H	2.61851800	6.02187100	-2.85058500
H	4.37866000	1.67161800	2.43528200
H	1.78852300	-0.81149600	3.47072400
H	4.52621500	-3.11061300	-1.19122000
H	6.02187100	-2.61851800	-2.85058500
H	1.67161800	-4.37866000	2.43528200
H	-1.78852300	0.81149600	3.47072400
H	-4.52621500	3.11061300	-1.19122000
H	-6.02187100	2.61851800	-2.85058500
H	-1.67161800	4.37866000	2.43528200
H	-0.81149600	-1.78852300	3.47072400
H	-3.11061300	-4.52621500	-1.19122000
H	-2.61851800	-6.02187100	-2.85058500
H	-4.37866000	-1.67161800	2.43528200
H	-0.01910300	5.42224100	-0.25471300
H	4.33026900	2.11083900	0.44911200
H	2.11083900	-4.33026900	0.44911200
H	-4.33026900	-2.11083900	0.44911200
H	-5.42224100	-0.01910300	-0.25471300
H	5.42224100	0.01910300	-0.25471300
H	0.01910300	-5.42224100	-0.25471300
H	-2.11083900	4.33026900	0.44911200
H	3.49676000	2.32107900	4.61746900
H	4.15909100	0.67355300	4.63667500
H	2.41433500	0.92840200	4.65894000
H	-3.49676000	-2.32107900	4.61746900
H	-4.15909100	-0.67355300	4.63667500
H	-2.41433500	-0.92840200	4.65894000
H	-2.32107900	3.49676000	4.61746900
H	-0.67355300	4.15909100	4.63667500
H	-0.92840200	2.41433500	4.65894000
H	2.32107900	-3.49676000	4.61746900
H	0.67355300	-4.15909100	4.63667500
H	0.92840200	-2.41433500	4.65894000
C	-0.67043100	9.06657500	-2.66925300
H	-1.68577400	9.04819900	-2.26637800
H	-0.17113400	9.98896300	-2.34738900
H	-0.71687100	9.06478800	-3.75879700
C	9.06657500	0.67043100	-2.66925300
H	9.04819900	1.68577400	-2.26637800
H	9.98896300	0.17113400	-2.34738900
H	9.06478800	0.71687100	-3.75879700
C	-9.06657500	-0.67043100	-2.66925300
H	-9.04819900	-1.68577400	-2.26637800
H	-9.98896300	-0.17113400	-2.34738900
H	-9.06478800	-0.71687100	-3.75879700
C	0.67043100	-9.06657500	-2.66925300
H	1.68577400	-9.04819900	-2.26637800
H	0.17113400	-9.98896300	-2.34738900
H	0.71687100	-9.06478800	-3.75879700
N	-0.03673900	-7.87330100	-2.22541200
N	0.03673900	7.87330100	-2.22541200
N	7.87330100	-0.03673900	-2.22541200
N	-7.87330100	0.03673900	-2.22541200
H	-0.08132500	7.56528300	-1.27212700
H	7.56528300	0.08132500	-1.27212700
H	-7.56528300	-0.08132500	-1.27212700
H	0.08132500	-7.56528300	-1.27212700

AzaGlyNMe cavitand *trans*

Total energy = -3267.94214265 a.u.

	x	y	z
O	-1.24720300	4.79836100	-0.65133400
O	-4.69049200	1.49710500	-0.49292200
C	-1.82422700	3.66597000	-1.15463300
C	-2.99615400	3.13226000	-0.56640500
C	-3.56180800	1.95025300	-1.10745200
C	-2.99125400	1.32464200	-2.22873200
C	-1.82435700	1.89315500	-2.75586100
C	-1.21579300	3.04718600	-2.25549900
C	-3.62648300	3.75023400	0.58732000
N	-3.13645600	4.82267400	1.11411700
N	-3.75023400	5.35693300	2.20795400
C	-3.32890800	6.60906400	2.66686300
O	-2.38240600	7.21435000	2.18661700
C	-3.62462800	0.07257300	-2.84882300
C	-3.59142800	0.08722200	-4.39000100

O	-4.79836100	-1.24720300	-0.65133400
O	-1.49710500	-4.69049200	-0.49292200
C	-3.66597000	-1.82422700	-1.15463300
C	-3.13226000	-2.99615400	-0.56640500
C	-1.95025300	-3.56180800	-1.10745200
C	-1.32464200	-2.99125400	-2.22873200
C	-1.89315500	-1.82435700	-2.75586100
C	-3.04718600	-1.21579300	-2.25549900
C	-3.75023400	-3.62648300	0.58732000
N	-4.82267400	-3.13645600	1.11411700
N	-5.35693300	-3.75023400	2.20795400
C	-6.60906400	-3.32890800	2.66686300
O	-7.21435000	-2.38240600	2.18661700
C	-0.07257300	-3.62462800	-2.84882300
C	-0.08722200	-3.59142800	-4.39000100
O	4.79836100	1.24720300	-0.65133400
O	1.49710500	4.69049200	-0.49292200
C	3.66597000	1.82422700	-1.15463300
C	3.13226000	2.99615400	-0.56640500
C	1.95025300	3.56180800	-1.10745200
C	1.32464200	2.99125400	-2.22873200
C	1.89315500	1.82435700	-2.75586100
C	3.04718600	1.21579300	-2.25549900
C	3.75023400	3.62648300	0.58732000
N	4.82267400	3.13645600	1.11411700
N	5.35693300	3.75023400	2.20795400
C	6.60906400	3.32890800	2.66686300
O	7.21435000	2.38240600	2.18661700
C	0.07257300	3.62462800	-2.84882300
C	0.08722200	3.59142800	-4.39000100
O	1.24720300	-4.79836100	-0.65133400
O	4.69049200	-1.49710500	-0.49292200
C	1.82422700	-3.66597000	-1.15463300
C	2.99615400	-3.13226000	-0.56640500
C	3.56180800	-1.95025300	-1.10745200
C	2.99125400	-1.32464200	-2.22873200
C	1.82435700	-1.89315500	-2.75586100
C	1.21579300	-3.04718600	-2.25549900
C	3.62648300	-3.75023400	0.58732000
N	3.13645600	-4.82267400	1.11411700
N	3.75023400	-5.35693300	2.20795400
C	3.32890800	-6.60906400	2.66686300
O	2.38240600	-7.21435000	2.18661700
C	3.62462800	-0.07257300	-2.84882300
C	3.59142800	-0.08722200	-4.39000100
H	-1.36991900	1.41222500	-3.61552300
H	-4.52278600	3.26820800	0.98534300
H	-4.68034400	5.01973500	2.44263800
H	-4.68572400	0.08963700	-2.58436600
H	-1.41222500	-1.36991900	-3.61552300
H	-3.26820800	-4.52278600	0.98534300
H	-5.01973500	-4.68034400	2.44263800
H	-0.08963700	-4.68572400	-2.58436600
H	1.41222500	1.36991900	-3.61552300
H	3.26820800	4.52278600	0.98534300
H	5.01973500	4.68034400	2.44263800
H	0.08963700	4.68572400	-2.58436600
H	1.36991900	-1.41222500	-3.61552300
H	4.52278600	-3.26820800	0.98534300
H	4.68034400	-5.01973500	2.44263800
H	4.68572400	-0.08963700	-2.58436600
H	-1.78321600	5.12719600	0.12389200
H	-4.79965300	0.52595400	-0.58947800
H	-0.52595400	-4.79965300	-0.58947800
H	4.79965300	-0.52595400	-0.58947800
H	5.12719600	1.78321600	0.12389200
H	-5.12719600	-1.78321600	0.12389200
H	1.78321600	-5.12719600	0.12389200
H	0.52595400	4.79965300	-0.58947800
H	-4.07030000	0.99603500	-4.76732600
H	-4.13291000	-0.77900400	-4.78265000
H	-2.57884600	0.05426600	-4.80175300
H	4.07030000	-0.99603500	-4.76732600
H	4.13291000	0.77900400	-4.78265000
H	2.57884600	-0.05426600	-4.80175300
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H	-0.77900400	4.13291000	-4.78265000
H	0.05426600	2.57884600	-4.80175300
H	-0.99603500	-4.07030000	-4.76732600
H	0.77900400	-4.13291000	-4.78265000
H	-0.05426600	-2.57884600	-4.80175300
C	-3.68966800	8.30112600	4.40148000
H	-4.53124000	8.66838900	4.99318800
H	-2.82646100	8.13761700	5.05918700
H	-3.41705700	9.05588500	3.66296100
C	-8.30112600	-3.68966800	4.40148000
H	-8.66838900	-4.53124000	4.99318800
H	-8.13761700	-2.82646100	5.05918700
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C	8.30112600	3.68966800	4.40148000
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H	8.13761700	2.82646100	5.05918700
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H	2.82646100	-8.13761700	5.05918700
H	3.41705700	-9.05588500	3.66296100
N	4.09958000	-7.08634700	3.70689000
N	-4.09958000	7.08634700	3.70689000
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H	-4.63421400	6.41650300	4.24273000
H	-6.41650300	-4.63421400	4.24273000
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12c

Total energy = -8397.41625016 a.u.

	x	y	z
C	8.45700000	17.42100000	-24.96600000
C	7.19800000	17.95300000	-25.27600000
C	6.23200000	17.15100000	-25.89900000
C	6.52700000	15.81800000	-26.21400000
H	5.78800000	15.20600000	-26.69000000
C	7.78600000	15.28700000	-25.90700000
C	8.75200000	16.08900000	-25.28500000
O	6.89800000	19.31400000	-24.95500000
H	7.66200000	19.71900000	-24.53600000
O	10.03900000	15.54700000	-24.97500000
H	9.93800000	14.80800000	-24.37100000
C	9.51500000	18.30000000	-24.27400000
H	10.47800000	17.89700000	-24.04100000
N	9.22700000	19.56900000	-23.96100000
N	10.18200000	20.36500000	-23.31600000
H	11.08200000	19.98900000	-23.09700000
C	9.88900000	21.63100000	-22.99300000
O	10.74600000	22.34700000	-22.41500000
N	8.68500000	22.13200000	-23.28700000
H	8.00400000	21.56300000	-23.74500000
C	8.36400000	23.52400000	-22.93600000
H	7.60900000	23.24800000	-22.22900000
C	9.40100000	24.43400000	-22.25000000
H	8.91600000	25.31400000	-21.88500000
H	10.15600000	24.71100000	-22.95600000
C	10.05000000	23.67900000	-21.07600000
C	11.44000000	23.50800000	-21.03400000

H	12.05000000	23.90200000	-21.81900000
C	12.03000000	22.82100000	-19.96400000
H	13.09200000	22.69200000	-19.93300000
C	11.23000000	22.30500000	-18.93600000
H	11.68200000	21.78200000	-18.11900000
C	9.83900000	22.47600000	-18.97700000
H	9.22900000	22.08100000	-18.19300000
C	9.25000000	23.16200000	-20.04700000
H	8.18700000	23.29300000	-20.07800000
C	7.35400000	24.09000000	-23.95000000
O	6.52900000	23.32200000	-24.51200000
N	7.35300000	25.39600000	-24.23600000
H	8.00800000	26.00700000	-23.79100000
C	6.38900000	25.93600000	-25.20800000
H	6.54500000	26.95000000	-24.90800000
C	4.89000000	25.59800000	-25.11500000
H	4.55900000	25.72500000	-24.10600000
H	4.33600000	26.25000000	-25.75600000
H	4.73300000	24.58400000	-25.41700000
C	7.08400000	26.12500000	-26.56900000
O	6.45500000	25.89500000	-27.63400000
C	8.31200000	13.99100000	-26.55200000
H	9.35800000	13.89200000	-26.35400000
C	8.08200000	14.04400000	-28.07400000
H	7.03500000	14.14100000	-28.27400000
H	8.60300000	14.88400000	-28.48400000
C	8.61000000	12.74900000	-28.71900000
H	8.08800000	11.90900000	-28.31000000
C	8.38200000	12.80300000	-30.24100000
H	8.74900000	11.90300000	-30.68900000
H	7.33600000	12.90000000	-30.44200000
H	8.90300000	13.64300000	-30.65000000
C	10.11600000	12.60900000	-28.43000000
H	10.63700000	13.45000000	-28.83900000
H	10.27400000	12.57200000	-27.37200000
H	10.48300000	11.71000000	-28.87700000
C	6.72600000	11.80800000	-23.90000000
C	7.62500000	12.65100000	-24.56600000
C	7.56100000	12.78300000	-25.96000000
C	6.59600000	12.07100000	-26.68700000
H	6.54800000	12.17000000	-27.75200000
C	5.69700000	11.22800000	-26.01900000
C	5.76300000	11.09600000	-24.62700000
O	8.52000000	13.31200000	-23.89100000
H	8.56300000	13.22200000	-22.93600000
O	4.84800000	10.23300000	-23.94600000
H	4.16100000	9.95000000	-24.55500000
C	6.79200000	11.66500000	-22.36900000
H	6.10600000	11.01800000	-21.86200000
N	7.67500000	12.32700000	-21.69500000
N	7.72500000	12.20400000	-20.30200000
H	7.08200000	11.60100000	-19.82900000
C	8.63400000	12.89200000	-19.60300000
O	9.44500000	13.64800000	-20.19800000
N	8.68000000	12.77800000	-18.27100000
H	8.03600000	12.17700000	-17.79700000
C	9.67800000	13.53600000	-17.50500000
H	10.15800000	12.65800000	-17.12400000
C	10.71900000	14.42600000	-18.21000000
H	11.43100000	13.80900000	-18.71700000
H	10.22500000	15.05800000	-18.91800000
C	11.44300000	15.29500000	-17.16600000
C	12.50000000	14.75900000	-16.41800000
H	12.80200000	13.74400000	-16.57200000
C	13.15900000	15.55100000	-15.46800000
H	13.96400000	15.14200000	-14.89700000
C	12.76000000	16.88000000	-15.26700000
H	13.26500000	17.48600000	-14.54200000
C	11.70400000	17.41700000	-16.01400000
H	11.40200000	18.43200000	-15.86200000
C	11.04400000	16.62500000	-16.96500000
H	10.23800000	17.03400000	-17.53600000
C	9.08600000	13.93200000	-16.14000000
O	9.10100000	13.11300000	-15.18600000
N	8.55800000	15.14900000	-15.96700000
H	8.54700000	15.80100000	-16.72500000
C	7.99300000	15.52700000	-14.66400000
H	8.67800000	16.33500000	-14.52100000
C	8.06300000	14.57500000	-13.45600000
H	9.05600000	14.19000000	-13.36200000
H	7.80300000	15.11000000	-12.56600000
H	7.37800000	13.76600000	-13.60000000
C	6.78100000	16.45300000	-14.88100000
O	6.95500000	17.68400000	-15.07100000
C	4.39600000	10.72800000	-26.67400000
H	4.29900000	9.67400000	-26.51400000
C	4.43700000	11.01500000	-28.18600000
H	4.53500000	12.06800000	-28.34700000
H	3.53300000	10.66800000	-28.63900000
C	5.63900000	10.28600000	-28.81600000
H	6.54400000	10.63400000	-28.36400000
C	5.49800000	8.77000000	-28.58300000
H	4.59300000	8.42200000	-29.03400000
H	6.33300000	8.26300000	-29.02000000
H	5.47200000	8.57200000	-27.53100000
C	5.67600000	10.57200000	-30.32800000
H	4.77100000	10.22400000	-30.78000000
H	5.77300000	11.62600000	-30.49000000
H	6.51100000	10.06600000	-30.76700000
C	0.94000000	11.15600000	-25.19200000
C	2.20900000	10.63300000	-25.48300000
C	3.19300000	11.45600000	-26.04700000
C	2.90900000	12.79900000	-26.32200000
H	3.66100000	13.42800000	-26.75200000
C	1.64200000	13.32100000	-26.03500000
C	0.65700000	12.50000000	-25.46900000
O	2.47200000	9.38400000	-25.22800000
H	1.79800000	8.81900000	-24.84300000
O	-0.63600000	13.03400000	-25.17400000
H	-0.55000000	13.75000000	-24.54000000
C	-0.14300000	10.25500000	-24.57200000
H	-1.11100000	10.65800000	-24.35300000
N	0.11800000	8.97100000	-24.30600000
N	-0.88300000	8.15400000	-23.76700000
H	-1.78900000	8.53400000	-23.57900000
C	-0.63200000	6.86700000	-23.50500000
O	-1.53300000	6.13500000	-23.01800000
N	0.57800000	6.35800000	-23.75800000
H	1.29300000	6.93800000	-24.14900000
C	0.86100000	4.94700000	-23.45800000
H	1.56800000	5.18000000	-22.68900000
C	-0.22700000	4.01800000	-22.89100000
H	0.22500000	3.11600000	-22.53600000
H	-0.93200000	3.78400000	-23.66100000
C	-0.95200000	4.72100000	-21.72800000
C	-0.22400000	5.18000000	-20.62300000
H	0.83700000	5.04200000	-20.58500000
C	-0.88400000	5.82000000	-19.56400000
H	-0.32800000	6.17100000	-18.72100000
C	-2.27300000	6.00000000	-19.61100000
H	-2.77700000	6.48600000	-18.80300000
C	-3.00200000	5.54200000	-20.71700000
H	-4.06300000	5.68000000	-20.75200000
C	-2.34100000	4.90300000	-21.77600000
H	-2.89900000	4.55400000	-22.62000000
C	1.93200000	4.41800000	-24.43000000
O	2.79800000	5.20200000	-24.90000000
N	1.94200000	3.12600000	-24.77400000
H	1.25400000	2.50500000	-24.39900000
C	2.96400000	2.62000000	-25.70000000
C	4.45700000	2.93600000	-25.49000000
H	4.64300000	3.96200000	-25.73700000

H	4.71800000	2.76300000	-24.46800000
C	2.36200000	2.50000000	-27.11200000
O	3.06400000	2.77200000	-28.12000000
C	1.13800000	14.64000000	-26.65000000
H	0.08500000	14.73200000	-26.48200000
C	1.41800000	14.63700000	-28.16500000
H	0.91100000	13.81200000	-28.61900000
H	2.47000000	14.54700000	-28.33300000
C	0.91000000	15.95300000	-28.78300000
H	1.41600000	16.77900000	-28.32900000
C	1.18800000	15.94900000	-30.29700000
H	0.68200000	15.12300000	-30.75100000
H	0.83600000	16.86300000	-30.72700000
H	2.24100000	15.85800000	-30.46600000
C	-0.60500000	16.08200000	-28.53900000
H	-0.79800000	16.08400000	-27.48700000
H	-0.95800000	16.99700000	-28.96800000
H	-1.11100000	15.25600000	-28.99400000
C	2.63900000	16.72400000	-23.87400000
C	1.76200000	15.90600000	-24.59900000
C	1.86800000	15.82600000	-25.99300000
C	2.85200000	16.56400000	-26.66400000
H	2.93500000	16.50400000	-27.73000000
C	3.73100000	17.38200000	-25.93900000
C	3.62200000	17.46300000	-24.54400000
O	0.84800000	15.21900000	-23.97500000
H	0.77600000	15.27400000	-23.02000000
O	4.51500000	18.30100000	-23.80600000
H	5.21900000	18.60500000	-24.38300000
C	2.52200000	16.81000000	-22.34100000
H	3.19000000	17.43700000	-21.78800000
N	1.61800000	16.12300000	-21.72100000
N	1.51700000	16.19400000	-20.32600000
H	2.14200000	16.77900000	-19.80900000
C	0.58800000	15.47800000	-19.68400000
O	-0.20000000	14.74300000	-20.33500000
N	0.49700000	15.54100000	-18.35100000
H	1.12300000	16.12700000	-17.83600000
C	-0.52100000	14.75100000	-17.64300000
H	-1.01800000	15.61100000	-17.24400000
C	-1.53500000	13.88400000	-18.41200000
H	-2.23300000	14.51600000	-18.91900000
H	-1.01500000	13.28100000	-19.12900000
C	-2.28700000	12.97300000	-17.42500000
C	-1.78400000	11.70100000	-17.12100000
H	-0.87900000	11.36100000	-17.57500000
C	-2.47100000	10.87400000	-16.22100000
H	-2.08800000	9.90200000	-15.99000000
C	-3.65800000	11.31900000	-15.62500000
H	-4.18200000	10.68900000	-14.93800000
C	-4.16000000	12.59200000	-15.92900000
H	-5.06600000	12.93300000	-15.47400000
C	-3.47400000	13.42000000	-16.82900000
H	-3.85800000	14.39000000	-17.06100000
C	0.03400000	14.31000000	-16.27600000
O	-0.01200000	15.09600000	-15.29500000
N	0.56400000	13.09000000	-16.13100000
H	0.60000000	12.46400000	-16.91100000
C	1.09500000	12.67000000	-14.82700000
H	0.41100000	11.85300000	-14.73000000
C	0.98600000	13.58100000	-13.59000000
H	1.22300000	13.01900000	-12.71100000
H	1.66900000	14.39900000	-13.68700000
H	-0.01300000	13.95900000	-13.51300000
C	2.31800000	11.75800000	-15.04000000
O	2.15700000	10.53200000	-15.27200000
C	5.05000000	17.90600000	-26.53500000
H	5.14300000	18.95200000	-26.33200000
C	5.05500000	17.67700000	-28.05800000
H	4.96200000	16.63100000	-28.26200000
H	5.97300000	18.04100000	-28.47100000
C	3.87200000	18.43100000	-28.69400000
H	2.95400000	18.06800000	-28.28200000
C	3.87700000	18.20100000	-30.21700000
H	3.78400000	17.15500000	-30.42000000
H	3.05500000	18.72500000	-30.65900000
H	4.79500000	18.56400000	-30.63000000
C	4.00600000	19.93700000	-28.40300000
H	4.92400000	20.30000000	-28.81600000
H	3.18400000	20.46100000	-28.84500000
H	4.00300000	20.09800000	-27.34500000
H	5.04800000	2.30600000	-26.12100000
H	2.78100000	1.59500000	-25.45500000
N	1.09300000	2.10600000	-27.26700000
H	0.53500000	1.89000000	-26.46600000
C	0.52700000	1.99300000	-28.59600000
H	1.10000000	1.27000000	-29.17500000
C	-0.92500000	1.53200000	-28.53700000
C	0.56000000	3.33100000	-29.32100000
H	-0.97700000	0.55600000	-28.05300000
H	-1.51300000	2.25100000	-27.96800000
C	-1.60200000	1.38400000	-29.87800000
O	0.10800000	3.42400000	-30.49300000
C	-2.93700000	0.96500000	-29.94600000
C	-0.89700000	1.66600000	-31.05500000
H	-3.48600000	0.74600000	-29.03100000
C	-3.56600000	0.82900000	-31.19000000
C	-1.52600000	1.53000000	-32.29800000
H	0.14100000	1.99200000	-31.00200000
H	-4.60400000	0.50300000	-31.24200000
C	-2.86000000	1.11100000	-32.36600000
H	-0.97600000	1.75000000	-33.21300000
H	-3.34900000	1.00500000	-33.33400000
N	3.55300000	12.26800000	-14.97500000
H	3.68300000	13.24200000	-14.78800000
C	4.70300000	11.40900000	-15.17500000
H	4.70400000	10.62000000	-14.42300000
C	4.67200000	10.76500000	-16.55700000
C	6.00000000	12.19600000	-15.05800000
H	3.63800000	10.61000000	-16.86400000
H	5.16900000	11.41700000	-17.27400000
C	5.35400000	9.42100000	-16.65000000
O	5.96900000	13.43000000	-14.81500000
C	5.38800000	8.73600000	-17.87000000
C	5.95400000	8.86100000	-15.51600000
H	4.92100000	9.17200000	-18.75400000
C	6.02100000	7.49000000	-17.95600000
C	6.58700000	7.61500000	-15.60200000
H	5.92800000	9.39500000	-14.56600000
H	6.04700000	6.95600000	-18.90600000
C	6.62100000	6.93000000	-16.82200000
H	7.05300000	7.17900000	-14.71800000
H	7.11400000	5.96000000	-16.88900000
N	5.54400000	15.94700000	-14.86700000
H	5.40500000	14.96700000	-14.71600000
C	4.40300000	16.81600000	-15.07000000
H	4.38300000	17.57800000	-14.29100000
C	4.47300000	17.50800000	-16.42700000
C	3.10000000	16.03100000	-15.01500000
H	5.51600000	17.66900000	-16.69900000
H	3.99300000	16.88300000	-17.17900000
C	3.79600000	18.85800000	-16.49100000
O	3.12100000	14.78900000	-14.81300000
C	3.20000000	19.28500000	-17.68300000
C	3.76700000	19.68000000	-15.35900000
H	3.22300000	18.64400000	-18.56400000
C	2.57400000	20.53500000	-17.74200000
C	3.14100000	20.93000000	-15.41800000
H	4.23200000	19.34700000	-14.43100000
H	2.10800000	20.86800000	-18.67000000
C	2.54400000	21.35800000	-16.61000000
H	3.11700000	21.57100000	-14.53700000

H	2.05600000	22.33200000	-16.65600000
N	8.35700000	26.53600000	-26.61900000
H	8.85600000	26.72000000	-25.77300000
C	9.01000000	26.71300000	-27.89900000
H	8.47100000	27.45800000	-28.48400000
C	10.45000000	27.18300000	-27.72100000
C	9.04100000	25.40900000	-28.68400000
H	10.45900000	28.13600000	-27.19200000
H	11.00600000	26.44300000	-27.14500000
C	11.21600000	27.39600000	-29.00500000
O	9.57200000	25.37200000	-29.82400000
C	12.54700000	27.82800000	-28.96300000
C	10.59400000	27.16200000	-30.23800000
H	13.03100000	28.01000000	-28.00300000
C	13.25700000	28.02500000	-30.15400000
C	11.30400000	27.35900000	-31.42800000
H	9.55800000	26.82600000	-30.27000000
H	14.29300000	28.36100000	-30.12100000
C	12.63500000	27.79100000	-31.38600000
H	10.82000000	27.17700000	-32.38800000
H	13.18800000	27.94500000	-32.31300000
N	1.12000000	4.51600000	-28.65400000
N	1.81600000	16.72400000	-15.19600000
N	7.29100000	11.51400000	-15.22900000
N	8.45100000	24.19200000	-28.10900000
H	7.69100000	24.26100000	-27.46200000
H	1.79800000	17.66000000	-15.54900000
H	7.32100000	10.58600000	-15.60400000
H	1.80000000	4.40500000	-27.92900000
H	0.84700000	5.34800000	-28.90000000
H	8.06300000	11.93400000	-14.99400000
H	1.03700000	16.30200000	-14.98600000
H	8.77700000	23.37400000	-28.34100000

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