SUPPORTING INFORMATION

Synthesis, Structures, and Properties of Nine-, Twelve-, and Eighteen-Membered *N*-Benzyloxyethyl Cyclic α-Peptoids

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List of abbreviations

Boc: *tert*-butoxycarbonyl

BOP-Cl: Bis(2-oxo-3-oxazolidinyl)phosphonic chloride

CIP: 2-chloro-1,3-dimethylimidazolinium hexafluorophosphate

DPPA: diphenylphosphorylazide

FDPP: pentafluorophenyldiphenylphosphinate

Fmoc: 9-fluorenylmethoxycarbonyl

HATU: O-(7-azabenzotriazol-1-yl)-*N*,*N*,*N*',*N*'-tetramethyluronium hexafluorophosphate

HFIP: hexafluoroisopropanol

PyBOP: benzotriazole-1-yl-oxy-tris-pyrrolidinophosphonium hexafluorophosphate

PyBrOP: bromo-tris-pyrrolidinophosphonium hexafluorophosphate

RP HPLC: reversed-phase high-performance liquid chromatography

TCDE: tetrachlorodideuteroethane

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General procedures

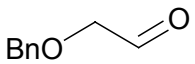
All reactions involving air or moisture sensitive reagents were carried out under a dry argon or nitrogen atmosphere using freshly distilled solvents. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under argon. Toluene and CH_2Cl_2 were distilled from CaH_2. Glassware was flame-dried (0.05 Torr) prior to use. When necessary, compounds were dried in vacuo over P_2O_5 or by azeotropic removal of water with toluene under reduced pressure. Starting materials and reagents purchased from commercial suppliers were generally used without purification unless otherwise mentioned. Reaction temperatures were measured externally; reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light, I_2, or by spraying with H_2SO_4-$Ce(SO_4)_2$, phosphomolybdic acid or ninhydrin solutions and drying. Flash chromatography was performed on Merck silica gel 60 (particle size: 0.040-0.063 mm) and the solvents employed were of analytical grade. HPLC analysis were performed on a C_{18} reversed-phase analytical and preparative columns (Waters, μBondapak, 10 μm, 125Å 3.9 mm × 300 mm and 7.8 × 300 mm respectively) using an Agilent 1100 series liquid chromatograph (Hewelett-Packard, Palo Alto, CA), equipped with a G-1312A binary pump, a G-1328B rheodyne injector, and a G-1365B multiple wavelength detector set at 220 nm. Yields refer to chromatographically and spectroscopically (^{1}H- and ^{13}C-NMR) pure materials. The NMR spectra were recorded on Bruker DRX 400, (^{1}H at 400.13 MHz, ^{13}C at 100.03 MHz), Bruker DRX 250 (^{1}H at 250.13 MHz, ^{13}C at 62.89 MHz), and Bruker DRX 300 (^{1}H at 300.1 MHz, ^{13}C at 75.5 MHz) spectrometers. Chemical shifts (δ) are reported in ppm relatively to the residual solvent peak ($CHCl_3$, δ = 7.26, $^{13}CDCl_3$, δ: = 77.0; CD_2HOD, δ = 3.34, $^{13}CD_3OD$, δ = 49.0; CD_2HCN: δ = 1.98; $^{13}CD_3CN$: δ = 1.39; $^{13}CCD_2Cl_4$: δ = 72.1; C_2DHCl_4: δ = 5.80; $^{13}CCD_2Cl_4$: δ = 72.1; CD_2HCOCD_3, δ = 2.05, $^{13}CD_3COCD_3$, δ = 30.0; ^1H-DMSO, δ = 2.50, ^{13}C-DMSO, δ = 39.5) and the multiplicity of each signal is designated by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; m, multiplet; br, broad. Coupling costants (*J*) are quoted in Hz. Homonuclear decoupling, COSY-45 and DEPT experiments completed the full assignment of each signal. High resolution ESI-MS spectra were performed on a Q-Star Applied Biosystem mass spectrometer. ESI-MS analysis in positive ion mode was performed using a Finnigan LCQ Deca ion trap mass spectrometer (ThermoFinnigan, San Josè, CA, USA) and the mass spectra were acquired and processed using the Xcalibur software provided by Thermo Finnigan. Samples were dissolved in 1:1 CH_3OH/H_2O, 0.1 % formic acid, and infused in the ESI source by using a syringe pump; the flow rate was 5 μl/min. The capillary voltage was set at 4.0 V, the spray voltage at 5 kV, and the tube lens offset at -40 V. The capillary temperature was 220 °C. Data were acquired in $MS^1$and MS^n scanning modes. Zoom scan was used in these experiments.

1.0 Synthesis

1.1 Synthetic procedures

Compound 6

To a solution of oxalyl chloride (5.84 g, 46.0 mmol) in anhydrous DCM (100 ml), at -78 °C and under nitrogen atmosphere, methyl sulfoxide (6.53 ml, 92.0 mmol) was added. After 15 minutes 2-benzyloxy-1-ethanol (5.82 g, 38.3 mmol) was added via cannula and the reaction mixture was stirred at -78 °C for 45 minutes. After the addition of triethylamine (32 ml, 230 mmol), the solution was stirred for 20 minutes at -78 °C and for further 20 minutes at r.t.. The mixture was treated with sat. aq. $NaHCO_3$ and the aqueous layer was extracted three times with DCM. The combined organic phases were dried over Na_2SO_4, filtered and evaporated to dryness. The crude residue was flash-chromatographed (10% - 50% ethyl ether in petroleum ether) to give pure **5** (4.42 g, 77%) as a viscous oil.

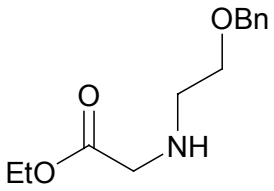


5

5: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.09 (2H, s, -C*H*$_2$CO); 4.63 (2 H, s, C*H*$_2$O); 7.27-7.34 (5H, m, Ar-H).

ESI MS: 151.2 m/z [M+H$^+$]

To a solution of **5** (0.529 g, 3.53 mmol) in CH_2Cl_2 (27 ml), **4** (0.591 g, 4.24 mmol), triethylamine (0.74 ml, 5.30 mmol) and $NaBH(OAc)_3$ (1.124 g, 5.30 mmol) were added. The reaction mixture was stirred at r.t. overnight, quenched with $NaHCO_3$ saturated solution and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated in vacuo. The crude residue was flash-chromatographed (2% of methanol in ethyl ether) to give **6** (0.582 g, 70% yield) and the related *bis*-adduct **6a** (0.092 g, 7 % yield) as a viscous oils.

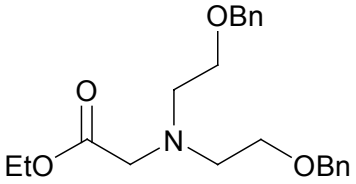


6

6: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (3H, t, *J* = 7.1 Hz, -CH_3); 2.04 (1 H, s, -NH); 2.82 (2H, t, *J* = 5.1 Hz, -NC*H*$_2$CH$_2$OBn); 3.41(2H, s, -OCCH$_2$N); 3.57 (2H, t, *J* = 5.1 Hz, -CH$_2$OBn); 4.16 (2H, q, *J* = 7.1 Hz, -OCH$_2$CH$_3$); 4.51 (2H, s, -OCH$_2$-Ar); 7.24-7.32 (5H, m, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 48.7, 50.8, 60.5, 69.4, 72.9, 127.5, 127.6 (× 2), 128.2 (× 2), 138.0, 172.1.

ESI MS: 238.1 m/z [M+H$^+$].



6a

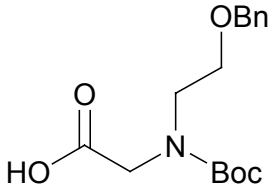
6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (3H, t, *J* = 7.1 Hz, -CH_3); 3.04 (4H, t, *J* = 5.7 Hz, -NC*H*$_2$CH_2OBn); 3.61 (2H, s, -OCCH_2N); 3.64 (2H, t, *J* = 5.7 Hz, -NCH$_2$C*H*$_2$OBn); 4.15 (2H, q, *J* = 7.1 Hz, -OCH_2CH$_3$); 4.55 (4H, s, -OCH_2-Ar); 7.31-7.38 (10H, m, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.0, 54.1 (× 2), 55.8, 60.0, 68.9 (× 2), 72.9 (× 2), 127.6 (× 6), 128.3 (× 4), 138.0 (× 2), 171.5.

ESI MS: 372.5 m/z [M+H$^+$].

Compound 7

To a stirred solution of **6** (0.106 g, 0.44 mmol) in THF (1.5 mL), at 0 °C, a solution of LiOH·H_2O (0.028 g, 0.67 mmol) in water (1.5 mL) was added. After 1 h at 0 °C, $NaHCO_3$ (0.056 g, 0.67 mmol) was added, followed by small portion addition of Boc_2O (0.146 g, 0.67 mmol). The resulting mixture was warmed at r.t. and stirred for additional 12 h. Then a saturated solution of $KHSO_4$ was added (till pH = 3) and the resulting mixture was concentrated in vacuo to half of its volume and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated in vacuo. The crude residue was flash-chromatographed [30-50% of ethyl ether in petroleum ether (1% AcOH)] to give **7** as a yellow oil (0.136 g, quant.).



7

7: ^{1}H NMR (400 MHz, TCDE, 80 °C) δ: 1.29 (9H, s, -C(CH_3)$_3$); 3.34 (2H, t, *J* = 5.2 Hz, -NC*H*$_2$CH_2OBn); 3.49 (2H, t, *J* = 5.1 Hz, -CH_2OBn); 3.84 (2H, s, -OCCH_2N); 4.37 (2H, s, -OCH_2Ar); 7.13-7.20 (5H, m, Ar-H).

^{13}C NMR (100 MHz, TCDE, 80 °C) δ: 26.4 (× 3), 47.1, 49.4, 66.9, 71.5, 79.3, 125.9 (× 2), 126.1, 126.7 (× 2), 135.8, 156.0, 169.8.

ESI MS: 310.2 m/z [$M+H^+$].

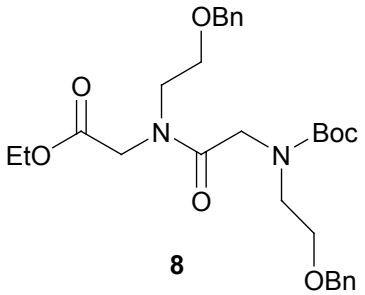
Method A (coupling): To a stirred solution of amine (1 mmol) and acid (1.2 mmol) in dry CH_2Cl_2 (10 mL) at r.t., BOP-Cl (1.3 mmol) and NEt_3 (2.6 mmol) were added. After 5 h, 1 N HCl solution (6 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phases were washed with $NaHCO_3$ saturated solution, dried (Na_2SO_4) and concentrated in vacuo. The crude residue was flash-chromatographed to give the pure product.

Method B (hydrolysis of the ester): To a stirred solution of ethyl ester peptoid (1 mmol) in THF (6 mL), at 0 °C, a solution of $LiOH·H_2O$ (3 mmol) in water (6 mL) was added. After 3 h at 0 °C, a saturated solution of $KHSO_4$ was added (till pH = 3) and the resulting mixture was concentrated in vacuo to half of its volume and extracted with ethyl acetate (3 × 50 mL). The combined organic phases were washed with water, dried (Na_2SO_4) concentrated in vacuo to give generally the pure acid, which was used without further purification.

Method C (Boc deprotection): To a stirred solution of Boc protected peptoid (1 mmol) in ethyl acetate (20 mL), a solution of 4 M HCl in dioxane (20 mL) was added. After 1 h the mixture was concentrated in vacuo washed with ethyl acetate and dried to give the pure hydrochloride, which was used without further purification.

Compound 8

6 (0.800 g, 3.37 mmol) and **7** (1.25 g, 4.06 mmol) were condensed using **Method A**. The crude residue was flash-chromatographed (50-90% of ethyl ether in petroleum ether) to give **8** as a yellow oil (67% yield).



8

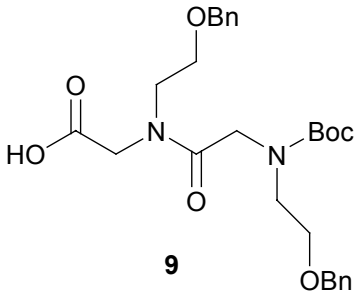
8: ^{1}H NMR (400 MHz, TCDE, 100 °C) δ: 1.10 (3H, t, J = 7.1 Hz, -CH_3); 1.29 (9H, s, -C(CH_3)$_3$); 3.35 (2H, t, J = 5.3 Hz, -NCH_2CH$_2$OBn); 3.43-3.51 (6H, t, J = 5.1 Hz, -NCH_2CH$_2$OBn, -NCH$_2$CH_2OBn, overlapped); 3.96 (2H, s, -OCCH$_2$N); 3.98-4.04 (4H, m, -OCCH$_2$N, -OCH_2CH$_3$, overlapped); 4.33 (4H, bs, -OCH$_2$Ar); 7.13-7.17 (5H, m, Ar-H).

^{13}C NMR (100 MHz, TCDE, 100 °C) δ: 12.2, 26.6 (× 3), 46.0 (× 2), 46.3, 47.4, 59.2, 67.0, 67.3, 71.2, 71.5, 78.1, 125.6 (× 3), 125.7 (× 2), 125.8, 126.4 (× 2), 126.5 (× 2), 136.3, 136.9, 153.7, 167.2, 167.8.

ESI MS: 551.2 m/z [M+Na$^+$].

Compound 9

8 (0.550 g, 1.04 mmol) was hydrolyzed using **Method B**, to give **9** as a yellow oil (0.478 g, 92%).



9

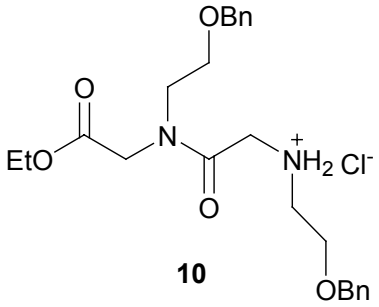
9: ^{1}H NMR (300 MHz, TCDE, 80 °C) δ: 1.28 (9H, s, -C(C*H*$_3$)$_3$); 3.30 (2H, t, *J* = 5.3 Hz, -NC*H*$_2$CH$_2$OBn); 3.43-3.46 (6H, t, *J* = 5.1 Hz, -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 3.96 (2H, bs, -OCCH$_2$N); 4.00 (2H, bs, -OCCH$_2$N); 4.32 (4H, s, -OCH$_2$Ar); 7.11-7.19 (5H, m, Ar-H).

^{13}C NMR (75 MHz, TCDE, 100 °C) δ: 12.2, 26.6 (× 3), 46.2 (× 2), 46.9, 47.6, 59.2, 66.4, 67.4, 71.2, 71.8, 78.5, 125.7 (× 3), 125.9 (× 2), 126.1, 126.5 (× 2), 126.7 (× 2), 135.8, 136.7, 153.8, 168.8 (× 2).

ESI MS: 501.2 m/z [M+H$^+$].

Compound 10

(0.683 g, 1.30 mmol) was deprotected using **Method C**, to give **10** as a yellow oil (0.556 g, quant.).



10

10: ^{1}H NMR (250 MHz, TCDE, 100 °C) δ: 1.09 (3H, s, -CH$_3$); 3.30 (2H, t, *J* = 5.3 Hz, -NC*H*$_2$CH$_2$OBn); 3.46-3.62 (8H, m -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 3.87-4.02 (6H, m, -

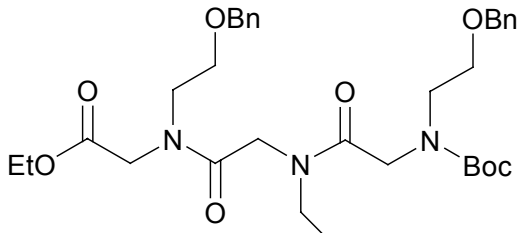
OCCH$_2$N, -OC*H*$_2$CH$_3$, overlapped) ; 4.32 (2H, s, -OCH$_2$Ar); 4.41 (2H, s, -OCH$_2$Ar); 7.13-7.17 (5H, m, Ar-H).

^{13}C NMR (75 MHz, TCDE, 100 °C) δ: 12.4, 44.5, 47.2 (× 2), 49.8, 60.0, 63.7, 66.1, 71.5, 71.9, 125.8 125.9, 126.1 (× 4), 126.7 (× 4), 135.6, 136.3, 164.6, 166.4.

ESI MS: 429.2 m/z [M+H$^+$].

Compound 11

6 (0.726 g, 3.06 mmol) and **9** (1.27 g, 2.55 mmol) were condensed using **Method A**, to give **11** as a yellow oil (1.06 g, 58%).



11

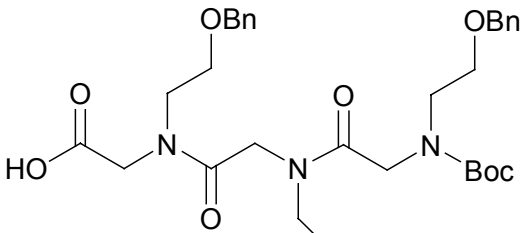
11: ^{1}H NMR (250 MHz, DMSO-d_6 120 °C, mixture of rotamers) δ: 1.19 (3H, s, -CH$_3$); δ: 1.28 (9H, s, -C(C*H*$_3$)$_3$); 3.38 (2H, t, *J* = 6.1 Hz, -NC*H*$_2$CH$_2$OBn); 3.45 (2H, t, *J* = 6.1 Hz, -NC*H*$_2$CH$_2$OBn); 3.51-3.65 (8H, m -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 4.03-4.27 (8H, m, -OCCH$_2$N, -OC*H*$_2$CH$_3$, overlapped), 4.47-4.56 (6H, s, -OCH$_2$Ar); 7.28-7.37 (15H, m, Ar-H).

^{13}C NMR (63 MHz, DMSO-d_6, 100 °C) δ: 13.1, 27.4 (× 3), 46.6 (bs × 5), 48.0, 59.9, 66.9, 67.3, 67.5, 71.5, 71.8 (× 2), 78.3, 126.6 (bs × 9), 127.4 (bs × 6), 137.7 (× 3), 154.5, 168.0 168.2, 168.6.

ESI MS: 720.4 m/z [M+H$^+$].

Compound 12

11 (1.20 g , 1.67 mmol) was hydrolyzed using **Method B**, to give **11a** as a yellow oil (0.877 g, 76%).



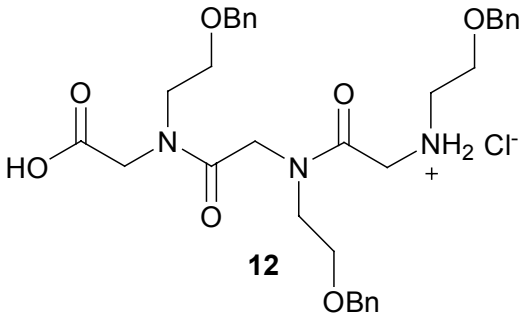
11a

11a: ^{1}H NMR (250 MHz, TCDE, 100 °C, mixture of rotamers) δ: 1.29 (9H, s, -C(C*H*$_3$)$_3$); 3.32-3.99 (12H, m, -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 4.10-4.32 (4H, m, -OCCH$_2$N); 4.34-4.49 (8H, m, OCCH$_2$N, -OCH$_2$Ar, overlapped); 7.09-7.21 (15H, m, Ar-H).

^{13}C NMR (63MHz, CDCl$_3$, 50 °C, mixture of rotamers) δ: 28.3 (× 3), 47.5 (bs), 47.8 (bs), 48.0 (bs), 48.7 (bs),49.0 (bs), 50.0 (bs), 67.6, 68.0 (bs), 68.4, 69.0 (bs), 69.5 (bs), 72.7, 73.0, 73.1,73.2, 73.4, 80.0, 127.4 (bs), 127.5 (bs), 127.6 (bs), 127.8 (bs), 128.2 (bs), 128.4 (bs); 138.0 (bs), 138.5, 155.9, 169.5, 170.1 (bs), 170.4 (bs), 172.1.

ESI MS: 714.3 m/z [M+Na$^+$].

11a (0.112 g e 0.162 mmol) was deprotected using **Method C**, to give **12** as a yellow oil (0.095 g, quant.).



12

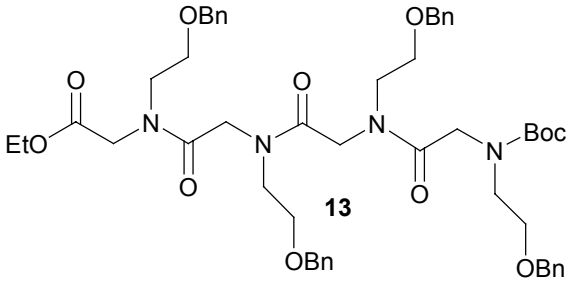
12: ^{1}H NMR (400 MHz, CDCl$_3$, mixture of rotamers) δ: 2.84-4.62 (24H, m), 7.26-7.39 (15H, m, Ar-H).

^{13}C NMR (63 MHz, CDCl$_3$, mixture of rotamers) δ: 47.1, 47.3, 47.5, 47.9, 48.0, 50.2, 51.8, 52.0, 64.7, 65.2, 66.8, 67.8, 68.1, 68.3, 68.5, 72.9, 73.0, 127.5, 127.6, 127.8, 128.3, 128.4, 137.5, 138.0, 166.5, 167.4, 167.8, 168.6, 173.3, 173.7, 174.3.

ESI MS: 592.3 m/z [M+H$^+$].

Compound 13

9 (0.464 g, 0.928 mmol) and **10** (0.393 g, 0.920 mmol) were condensed using **Method A**. The crude residue was flash-chromatographed (1-6% of methanol in ethyl ether) to give **13** as a yellow oil (63% yield).



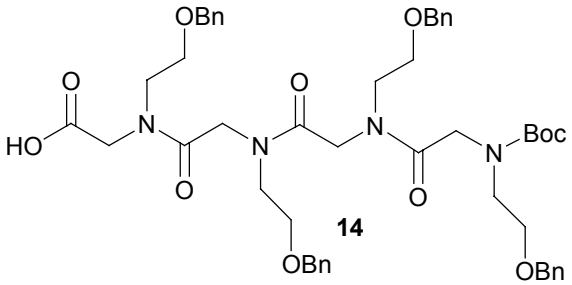
13: ^{1}H NMR (400 MHz, TCDE, 60 °C, mixture of rotamers) δ: 1.25 (3H, bt, J = 7.1 Hz, -CH_3); 1.46 (9H, bs, -C(CH_3)$_3$); 3.40-3.61 (16H, m, -NCH_2CH$_2$OBn, -NCH$_2$CH_2OBn, overlapped); 3.82-4.19 (8H, m, -OCCH$_2$N); 4.30 (2H, m, -OCH_2CH$_3$); 4.40-4.54 (8H, m, -OCH$_2$Ar); 7.30-7.33 (20H, m, Ar-H).

^{13}C NMR (75 MHz, TCDE, 100 °C) δ: 12.2, 26.6 (× 3), 46.1 (× 4), 46.6 (× 2), 47.4 (× 2), 59.4, 66.9 (× 2), 67.1 (× 2), 71.1, 71.5 (× 3), 77.9, 125.5 (× 2), 125.8 (× 10), 126.5 (× 8), 136.8 (× 4), 153.8, 167.1 (× 4).

ESI MS: 933.4 m/z [M+Na$^+$].

Compound 14

13 (0.132 g, 0.145 mmol) was hydrolyzed using **Method B**. The crude residue was flash-chromatographed (2-10% of methanol in CH_2Cl_2) to give **14** as a yellow oil (65% yield).



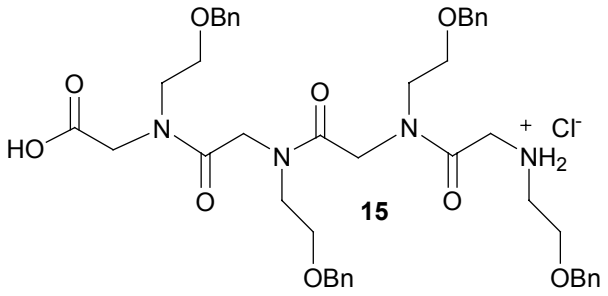
14: ^{1}H NMR (400 MHz, TCDE, 100 °C, mixture of rotamers) δ: 1.27 (9H, bs, -C(CH_3)$_3$); 3.32-3.50 (16H, m, -NCH_2CH$_2$OBn, -NCH$_2$CH_2OBn, overlapped); 3.89-4.09 (8H, m, -OCCH$_2$N); 4.28-4.35 (8H, m, -OCH$_2$Ar); 7.14 (20H, m, Ar-H).

^{13}C NMR (75 MHz, TCDE, 100 °C) δ: 26.6 (× 3), 46.0 (× 6), 47.4 (× 2), 66.4 (× 2), 67.1 (× 2), 71.2 (× 2), 71.4 (× 2), 78.2, 125.8 (× 12), 126.6 (× 8), 136.2 (× 2), 136.7 (× 2), 153.9, 167.5 (× 2), 168.1 (× 2).

ESI MS: 905.4 m/z [M+Na$^+$].

Compound 15

14 (0.371 g, 0.420 mmol) was deprotected using **Method C**, to give **15** as a yellow oil (0.328 g, quant.).



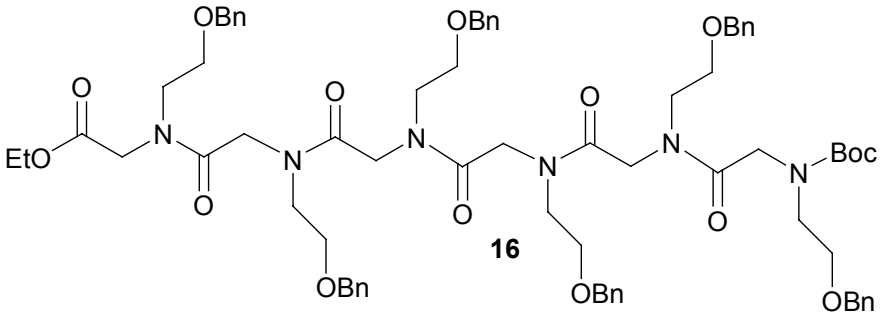
15: ^{1}H NMR (400 MHz, TCDE, 100 °C, mixture of rotamers) δ: 3.26-3.64 (16H, m, -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 3.70-4.07 (8H, m, -OCCH$_2$N) ; 4.19-4.50 (8H, m, -OCH$_2$Ar); 7.14 (20H, m, Ar-H).

^{13}C NMR (75 MHz, TCDE, 100 °C) δ: 46.8 (× 6), 48.5 (× 2), 66.4 (× 4), 71.9 (× 4), 125.9 (× 12), 126.6 (× 8), 135.5 (× 2), 136.2 (× 2), 164.7, 167.4 (× 2), 168.5.

ESI MS: 783.4 m/z [M+H^{+}].

Compound 16

To a stirred solution of **14** (0.031 g, 0.035 mmol) in dry CH$_3$CN (2 mL) **10** (0.020 g, 0.042 mmol) in dry CH$_3$CN (1 mL) was added and the resulting mixture was cooled to 0 °C. CIP (0.015 g, 0.053 mmol) and DIPEA (0.025 mL, 0.014 mmol) were added. The mixture was left at r.t. for 24 h and then it was treated with 1 N HCl solution (2 mL) and extracted with CH$_2$Cl$_2$ (3 × 15 mL).The combined organic phases were washed with NaHCO$_3$ satured solution, dried (Na$_2$SO$_4$) and concentrated in vacuo. The crude residue was flash-chromatographed (1-5 % of methanol in CH$_2$Cl$_2$) to give **16** as a yellow oil (0.025 g, 54% yield).



16: ^{1}H NMR (400 MHz, CDCl$_3$, mixture of rotamers) δ: 1.22 (3H, bt, *J* = 7.0 Hz, -C*H*$_3$); 1.39 (9H, bs, -C(C*H*$_3$)$_3$); 3.25-3.61 (24H, m, -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 4.00-4.13 (12H, m, -OCCH$_2$N); 4.20-4.70 (14H, m, -OC*H*$_2$CH$_3$, -OCH$_2$Ar, overlapped); 7.26-7.39 (30H, m, Ar-H).

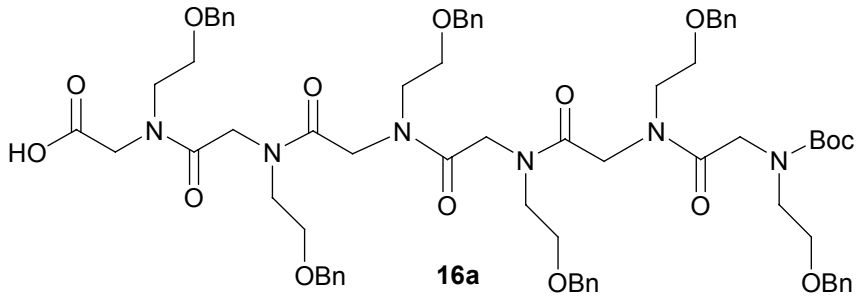
^{13}C NMR (75 MHz, CDCl$_3$) δ: 14.0, 28.2, 28.3, 46.5 (br), 47.0 (br), 47.3 (br), 47.7 (br), 48.3 (br), 48.5 (br), 48.8 (br), 49.0 (br), 50.0 (br), 50.4 (br), 61.0 (br), 61.3 (br), 67.2 (br), 68.0 (br), 68.6 (br), 69.0

(br), 69.1 (br), 69.5 (br), 72.7, 73.0, 73.2, 73.3, 79.6, 127.5, 127.8, 128.2, 129.5, 132.7 (br), 137.3 (br), 137.9 (br), 138.3 (br), 155.7 (br),166.2 (br), 168.4 (br), 168.7 (br), 169.1 (br), 169.5 (br), 170.1 (br).

ESI MS: 1293.6 m/z [M+H$^+$].

Compound 17

16 (0.080 g, 0.062 mmol) was hydrolyzed using **Method B**. The crude residue was flash-chromatographed (3-7% of methanol in CH_2Cl_2) to give **16 a** as a yellow oil (0.063 g, 80%).

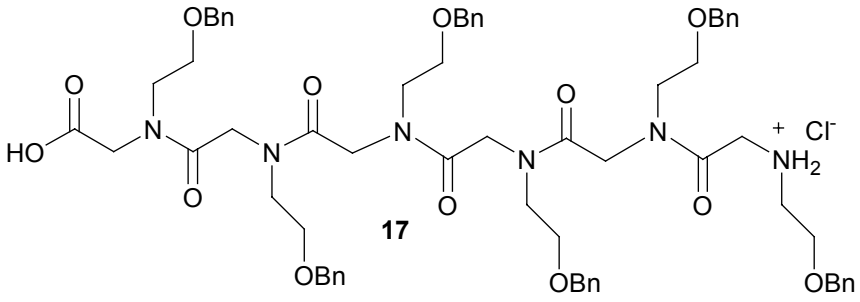


16a

16a: ^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ: 1.40 (9H, bs, -C(C*H*$_3$)$_3$); 3.40-3.64 (24H, m, -NC*H*$_2$CH$_2$OBn, -NCH$_2$C*H*$_2$OBn, overlapped); 3.90-4.10 (12H, m, -OCCH$_2$N); 4.20-4.70 (12H, m, -OCH$_2$Ar, overlapped); 7.26-7.39 (30H, m, Ar-H).

ESI MS: 1265.7 m/z [M+H$^+$].

16a (0.045 g, 0.036 mmol) was deprotected using **Method C**, to give **17** as a yellow oil (0.041 g, quant.).



17

^{1}H NMR (250 MHz, $CDCl_3$, mixture of rotamers) δ: 3.06-3.67 (26H, m), 3.88-4.58 (22H, m), 7.29 (30H, m, Ar-H).

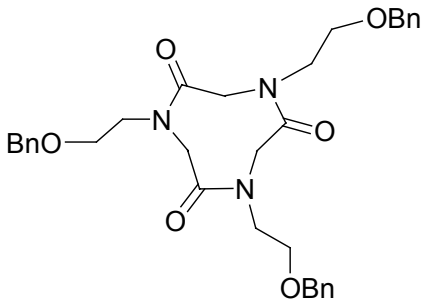
^{13}C NMR (75 MHz, $CDCl_3$) δ: 47.7 (br), 67.5, 67.4, 68.0, 68.3, 68.5, 68.9, 72.4, 72.7, 73.4, 73, 7, 127, 5, 127, 8 (br), 128.2 (br), 128.5, 137.5 (br), 138.0 (br), 168,6, 168.8 (br), 170.0 (br), 169.3, 169.5, 170.0.

ESI MS: 1165.6 m/z [M+H$^+$].

Compound 1

To a stirred solution of HATU (0.199 g, 0.524 mmol) and DIPEA (0.18 mL, 1.048 mmol) in dry DMF (40 mL) at r.t., a solution of **12** (0.100 g, 0.169 mmol) in dry DMF (40 mL) was added by syringe pump in 3 h. After 18 h the resulting mixture was concentrated in vacuo, diluted with CH_2Cl_2 (20 mL) and 0.5 N HCl solution (20 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 20 mL) and the combined organic phases were washed with 0.1 M $NaHCO_3$ (12 mL) and water (12 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude residue was flash-chromatographed (2-3 % of methanol in CH_2Cl_2) to give **1** as a yellow oil (0.015 g, 15 % yield).

Cyclization in the presence of FDPP (0.201 g, 0.524 mmol), PyBOP (0.273 g, 0.524 mmol), DPPA (0.144, 0.524 mmol), and PyBrOP (0.244 g, 0.524 mmol), in the same reaction conditions, gave a complex mixture of oligo- and cyclooligomers (RP-HPLC and ESI-MS analysis) and formation of low yields of **1** (<3%; yields evaluated after flash-chromatography purification).



1

1: ^{1}H NMR (400 MHz, $CDCl_3$, Figure S1) δ: 3.54-3.75 (9H, m, -NCH_2CH_2OBn, overlapped); 3.96 (3H, *J* = 15.4 Hz , -OCC*H*HN); 4.06 (3H, ddd, *J* = 14.0, 3.2, 3.2 Hz, -NCH_2CH_2OBn); 4.50 (6H, bs, -OCH_2Ar); 4.68 (3H, *J* = 15.4 Hz , -OCC*H*HN), 7.29-7.39 (15H, m, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 46.6 (× 3), 50.1 (× 3), 68.1 (× 3), 72.9 (× 3), 127.6 (× 9), 128.4 (× 6), 138.0 (× 3), 167.3 (× 3).

High temperature spectra: ^{1}H NMR (300 MHz, TCDE, 152 °C) δ: 3.56 (12H, bs, -NCH_2CH_2OBn); 4.13 (6H, bs, -$OCCH_2N$); 4.37 (6H, s, -OCH_2Ar); 7.16 (15H, bs, Ar-*H*).

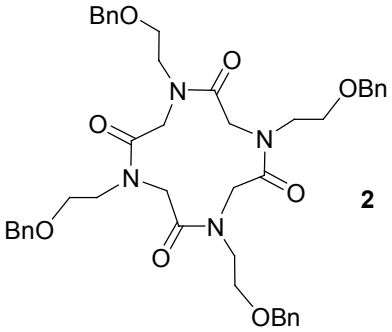
^{13}C NMR (75 MHz, TCDE, 152 °C) δ: 46.1 (× 3, br), 49.0 (× 3, br), 66.2 (× 3), 71.4 (× 3), 125.8 (× 9), 126.5 (× 6), 136.6 (× 3), 165.7 (× 3).

HR MS: $[M+H]^+$ m/z 574.2984 (calcd for $C_{33}H_{40}N_3O_6$ 574.2917).

Compound 2

To a stirred solution of **15** (0.116 g, 0.14 mmol) in dry DMF (67 mL) at r.t., DIPEA (0.073 mL, 0.42 mmol) and PyBOP (0.109 g, 0.21 mmol), or FDPP (0.080 g, 0.21 mmol) or PyBrOP (0.098 g, 0.21 mmol), were added. After 18 h the resulting mixture was concentrated in vacuo, diluted with CH_2Cl_2 (15 mL) and a 1 N HCl solution (15 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 15

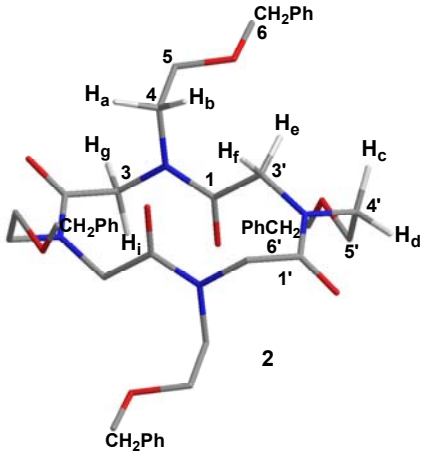
mL) and the combined organic phases were washed with 0.1 M $NaHCO_3$ (10 mL) and water (10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude residue was washed twice with petroleum ether/ethyl ether 1:1 and then flash-chromatographed (1-5 % of methanol in CH_2Cl_2) to give **2** as an amorphous solid (0.076 g, 65% yield both in the case of PyBOP and FDPP and no reaction in the case of PyBrOP, see HPLC analysis, paragraph 3.2). Compound **2** was obtained by slow evaporation of an acetone solution to give needle-like crystals (see paragraph 6.0 for the X-ray studies) m. p. = 202-204 °C .



2

2: ^{1}H NMR (300 MHz, TCDE, Figure S2) δ: 2.94 (4H, m, -NC*H*$_2$CH$_2$OBn, overlapped); 3.11 (2H, d, *J* = 14.6 Hz, -OCCH$_2$N); 3.25-3.41 (10H, m, -NCH$_2$C*H*$_2$OBn and -NC*H*$_2$CH$_2$OBn, overlapped); 3.74 (2H, ddd, *J* = 14.2, 4.5 Hz, -NCH$_2$C*H*$_2$OBn); 4.04 (2H, d, *J* = 17.5 Hz, -OCCH$_2$N); 4.12 (2H, d, *J* = 17.5 Hz, -OCCH$_2$N); 4.21 (8H, m, -OCH$_2$Ar); 5.05 (2H, d, *J* = 14.6 Hz, -OCCH$_2$N); 7.10 (20H, m, Ar-H).

Assignment of the proton and carbon resonances was achieved through ^{1}H-^{13}C DQF-COSY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC in $(CD_3)_2CO$:



^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ: 3.08 (2H, bd, *J* = 16.0 Hz, H$_a$); 3.21 (2H, m, H$_c$); 3.26 (2H, d, *J* = 14.5 Hz, H$_i$); 3.50-3.62 (8H, m, -NCH$_2$C*H*$_2$OBn, overlapped); 3.66 (2H, m, H$_b$); 3.82 (2H, ddd, *J* = 13.0, 4.3 Hz, H$_d$); 4.21 (2H, d, *J* = 17.9 Hz, H$_e$); 4.44 (4H, s, -OCH$_2$Ar); 4.46 (2H, d, *J* = 17.9 Hz, H$_f$); 4.48 (4H, s, -OCH$_2$Ar); 5.31 (2H, d, *J* = 14.5 Hz, H$_g$); 7.30 (20H, m, Ar-H).

^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ: 46.2 (C-4, × 2), 48.1 (C-3, × 2), 48.8 (C-4', × 2), 51.4 (C-3', × 2), 67.4 (C-5, × 2), 69.2 (C-5', × 2), 73.6 (C-6', 2), 73.7 (C-6, × 2), 128.4 (× 12), 129.0 (× 4), 129.3 (× 4), 139.5 (× 2), 140.1 (× 2), 167.6 (× 2), 170.8 (× 2).

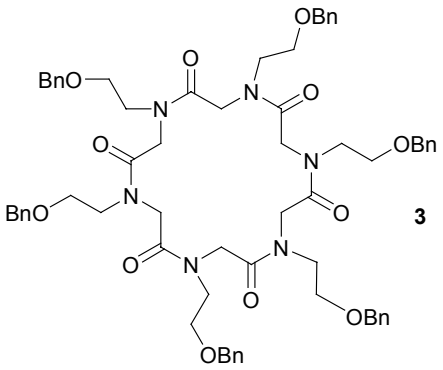
HR MS: $[M+H]^+$ m/z 765,3822 (calcd for $C_{44}H_{53}N_4O_8$ 765,3863).

Compound 3

To a stirred solution of **17** (0.45 g, 0.39 mmol) and DIPEA (0.42 mL, 2.40 mmol) in dry DMF (166 mL) at r.t., a solution of PyBOP (0.624 g, 1.20 mmol), or FDPP (0.461 g, 1.20 mmol), or PyBrOP (0.559 g, 1.20 mmol), in dry DMF (20 mL) was added by syringe pump in 4 h. After 18 h the resulting mixture was concentrated in vacuo, diluted with AcOEt (50 mL) and a 0.5 N HCl solution (50 mL) was added. The mixture was extracted with AcOEt (2 × 50 mL) and the combined organic phases were washed three times with water (25 mL), dried ($MgSO_4$) and concentrated in vacuo. See paragraph 3.2 for the HPLC chromatograms of the cyclizations in the presence of PyBOP, FDPP, or PyBrOP. The yields for the PyBOP and FDPP-induced cyclization were >97% (HPLC analysis, paragraph 3.2). The crude residue form the PyBOP-induced cyclization, was purified by HPLC on a C_{18} reversed-phase preparative column. A linear gradient of 40-100% acetonitrile in water (0.1% TFA) over 18 min was used with a flow rate of 2.0 mL/min, for further 2 min with a flow rate of 1.5 mL/min, and for the last 10 min with a flow rate of 1.0 mL/min (elution time: 23.2 min). The sample was dried in a falcon tube with a N_2 flow.

It must be noted that, because of the high affinity of **3** for metal cations, the silica-gel column chromatography of the crude from the cyclization, invariably yields **3** in a complexed form (we suppose that the silica gel used in the purification contains traces of metals enough to induce complexation of compound **3**) giving an ^{1}H-NMR spectrum very similar to that reported in Figure 3c. The only way to obtain free **3** is to purify it on HPLC (the presence of the TFA and the use of the reversed-phase column hampers the formation of possible complexes). **3** should always be collected in polypropylene tubes and stored in eppendorf vials or falcon tubes. If **3** enters in contact with glass (Pasteur pipettes or glass vials should always be avoided), complexation takes immediately place.

Compound **3** was crystallized as strontium complex from a 4.0 mM solution in acetonitrile:cloroform 9:1 (1.0 ml). To this solution, 2.0 equivalents of strontium picrate were gradually added. A yellow microcrystalline precipitate was readily formed. The mixture was left 12 hours at room temperature and the needle-like crystals were collected, washed twice with cold ethyl ether (0.5 ml) and dried under vacuum (see paragraph 6.0 for the X-ray studies).



3

3: ^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, mixture of rotamers, Figure S3) δ: 3.24-3.77 (26H, m); 3.85-4.15 (~4H, m); 4.40-4.61 (18H, m); 7.26-7.36 (30H, m, Ar-H) .

^{13}C NMR (100 MHz, CD_3CN, mixture of rotamers) δ: 47.0, 48.3, 49.0, 49.4, 49.9, 50.4, 50.9, 51.9, 52.0, 67.3, 67.5, 68.4, 69.0, 69.2, 73.4, 73.7, 73.9, 128.5, 128.9, 129.3, 129.4, 139.5, 139.8, 170.1, 170.5, 171.0, 172.3.

It must be noted that the low temperature ^{1}H NMR spectra (recorded till –70 °C, CD_2Cl_2 solution, 400 MHz) show an even more complex signals pattern.

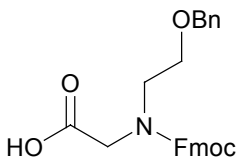
High temperature spectra: ^{1}H NMR (250 MHz, TCDE, 156 °C) δ: 3.39 (24H, bs, -NC*H*$_2$C*H*$_2$OBn); 3.92 (12H, bs, -OCC*H*$_2$N); 4.27 (12H, bs, -OC*H*$_2$Ar); 7.11 (30H, bs, Ar-*H*).

^{13}C NMR (75 MHz, TCDE, 120 °C) δ: 46.5 (× 6), 48.0 (× 6), 66.5 (× 6), 71.4 (× 6), 125.7 (× 18), 126.5 (× 12), 136.2 (× 6), 167.7 (× 6).

HR MS: $[M+Na]^+$ m/z 1169,5619 (calcd for $C_{66}H_{78}N_6NaO_{12}$ 1169,5575).

Compound 18

To a stirred solution of **6** (2.82 g, 11.9 mmol) in 1,4 dioxane (40 mL), at 0 °C, a solution of $LiOH·H_2O$ (0.75 g, 17.9 mmol) in water (1.5 mL) was added. After 1 h at 0 °C, $NaHCO_3$ (1.50 g, 17.9 mmol) was added, followed by small portion addition of FmocCl (4.63 g, 17.9 mmol). The resulting mixture was warmed at r.t. and stirred for additional 12 h. Then a saturated solution of $KHSO_4$ was added (till pH = 3) and the resulting mixture was concentrated in vacuo to half of its volume and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated in vacuo. The crude residue was flash-chromatographed [30-95% of ethyl ether in petroleum ether (1% AcOH)] to give **18** as a yellow oil (4.69 g, 91%).



18

18: ^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ: 3.38 (4H, m, NC*H*$_2$CH$_2$OBn); 3.58 (2H, t, *J* = 5.1 Hz, -CH$_2$OBn); 3.64 (2H, t, *J* = 5.1 Hz, -CH$_2$OBn); 4.07 (2H, s, -OCCH$_2$N); 4.15 (2H, s, -OCCH$_2$N); 4.23 (2H, m, -CHFmoc); 4.40 (2H, s, -OCH$_2$Ar); 4.45 (2H, d, *J* = 10.2 Hz, CH$_2$Fmoc); 4.48 (2H, s, -OCH$_2$Ar); 4.54 (2H, d, *J* = 10.2 Hz, CH$_2$Fmoc); 7.15-7.31 (22H, m, Ar-H); 7.32 (2H, m, Ar-H); . 7.31 (2H, m, Ar-H)..

ESI MS: 432.1 m/z [M+H$^+$].

1.2 Solid-phase synthesis of linear precursors 12, 15, 17

Linear peptide sequence was synthesized using standard manual Fomc solid-phase peptide synthesis protocols. 0.30 g of 2-chlorotrityl chloride resin (Fluka; 2,α-dichlorobenzhydryl-polystyrene crosslinked with 1% DVB; 100-200 mesh; 1.55 mmol/g) was swelled in dry DMF (3 mL) for 45 min and washed twice in dry DCM (3 mL). The first *N*-Fmoc *N*-alkylated glycine (**18**, 0.17 mmol) in dry DCM (3 mL) and DIPEA (0.68 mmol) were added on a shaker platform for 1.5 h at room temperature, followed by washing with dry DCM (3 mL) then twice with a mixture of DCM/MeOH/DIPEA (17:2:1) and finally with DMF (3 × 3 mL). Resin loaded with the first *N*-Fmoc *N*-alkylated glycine was incubated twice with 20% piperidine/DMF (v/v, 3 mL) on a shaker platform for 3 min and 7 min respectively, followed by extensive washes with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL). Note that, to avoid the formation of diketopiperazine, the deprotection of the second aminoacid was effected incubating twice with 20% piperidine/DMF (v/v, 3 mL) on a shaker platform for 3 min. The yields of loading step and of the following coupling steps were evaluated interpolating the absorptions of dibenzofulvene-piperidine adduct (λ_{max} = 301, ε = 7800 M^{-1} cm^{-1}), obtained in Fmoc deprotection step. After loading of the first monomer all subsequent *N*-Fmoc *N*-alkylated glycine addition and Fmoc deprotection steps were performed as follow, until the desired oligomer length was obtained. The resin was incubated with a solution of *N*-Fmoc *N*-alkylated glycine (0.68 mmol), HATU (or PyBOP) (0.66 mmol), DIPEA (1.36 mmol) in dry DMF (2 mL) on a shaker platform for 1 h, followed by extensive washes with DMF (3 × 3 mL), DCM (3 × 3 mL) and DMF (3 × 3 mL). Chloranil test was performed and once the coupling was complete the Fmoc group was deprotected with piperidine as described above and the resin washed again to prepare it for the next coupling. The oligomer-resin was cleaved in 4 mL of 20% HFIP in DCM (v/v). The cleavage was performed on a shaker platform for 30 min at room temperature the resin was then filtered away. The resin was treated again with 4 mL of 20% HFIP in DCM (v/v) for 5 min, washed twice with DCM (3 mL), filtered away and the combined filtrates were concentrated in vacuo. The final products were dissolved in 50% ACN in HPLC grade water and analysed by RP-HPLC and ESI mass spectrometry (see paragraph 3.1).

2.0 ^{1}H-NMR spectra and variable temperature experiments

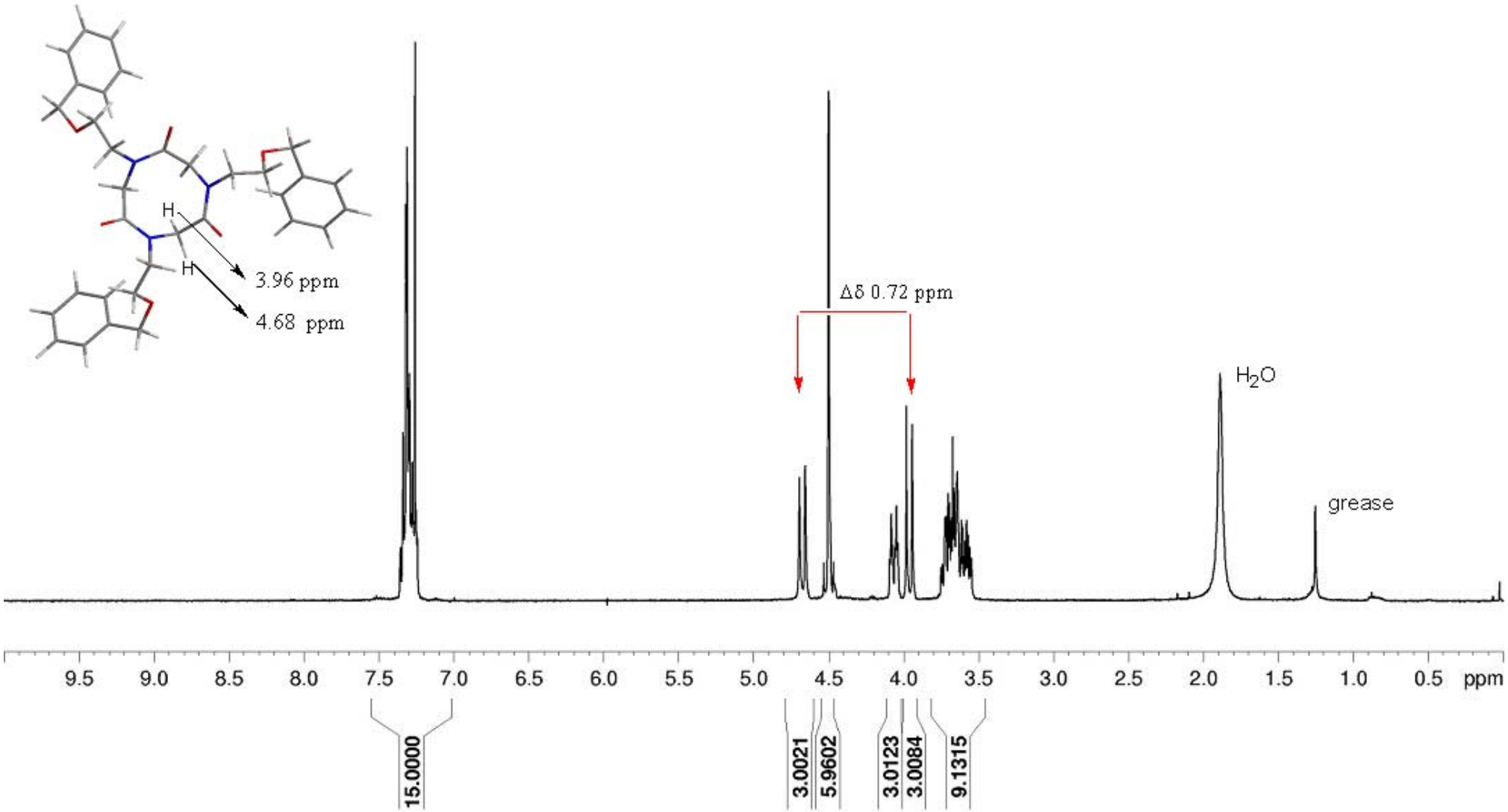


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of **1**

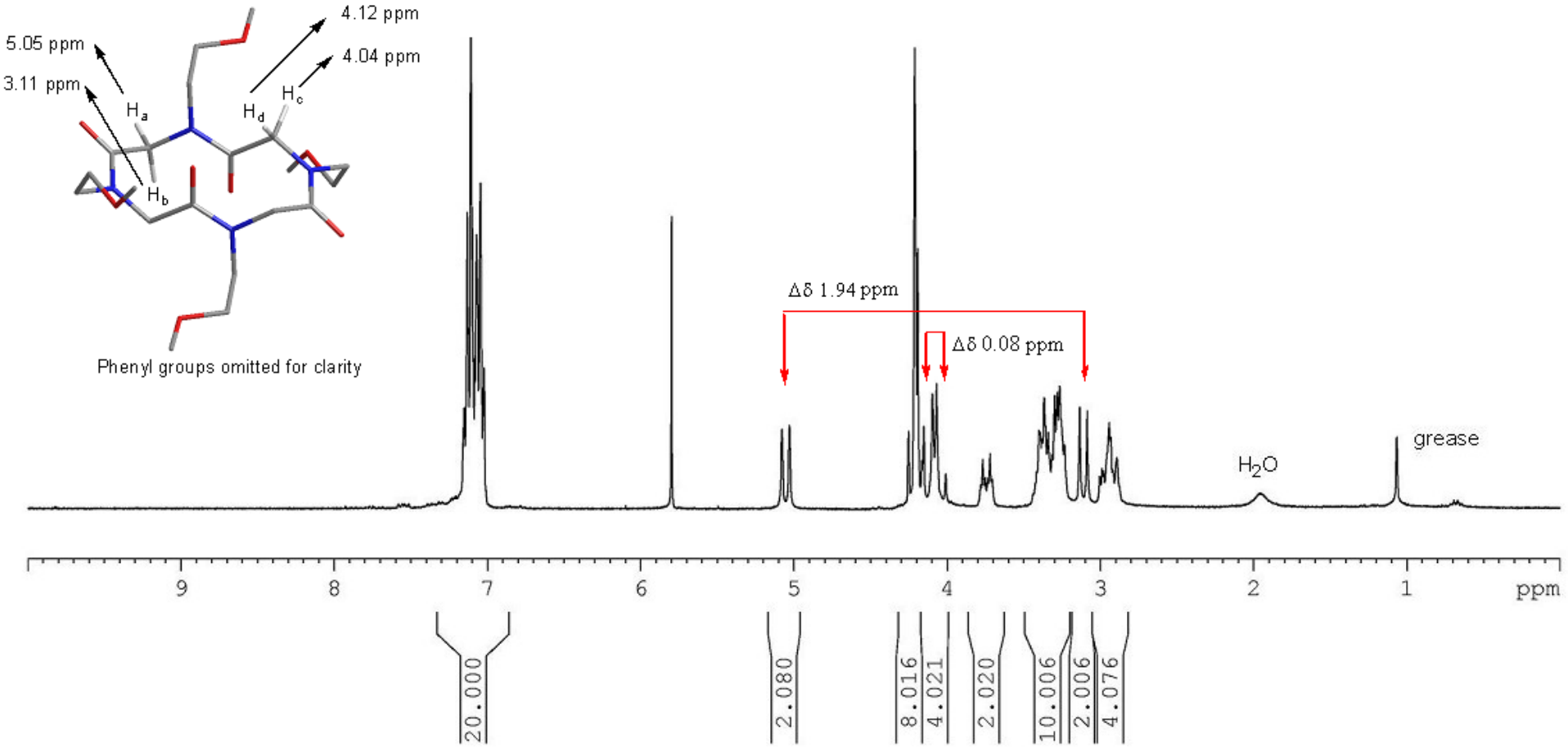


Figure S2. ^{1}H NMR (300 MHz, TCDE) of **2**

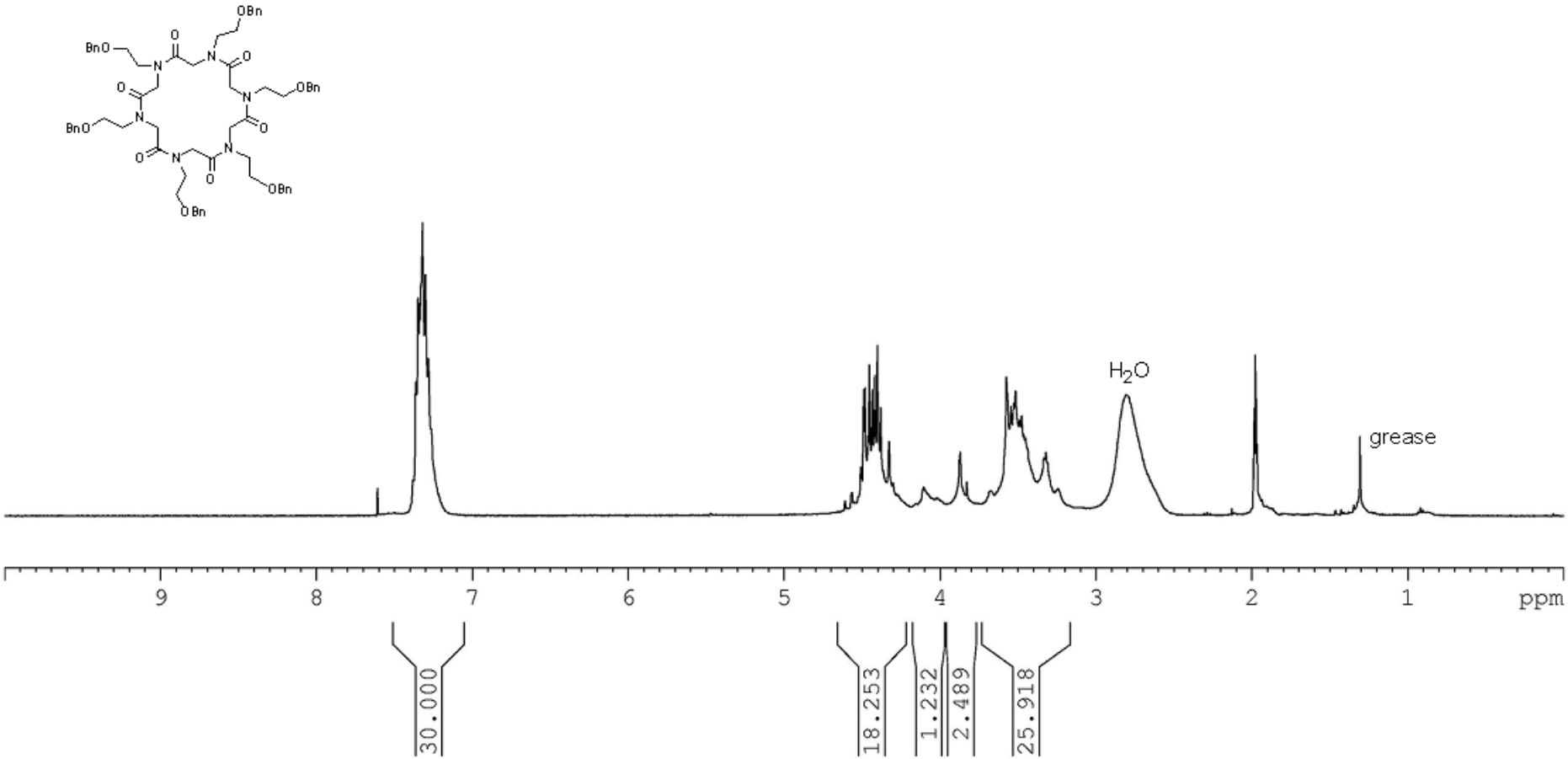


Figure S3. ^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, mixture of rotamers) of **3**

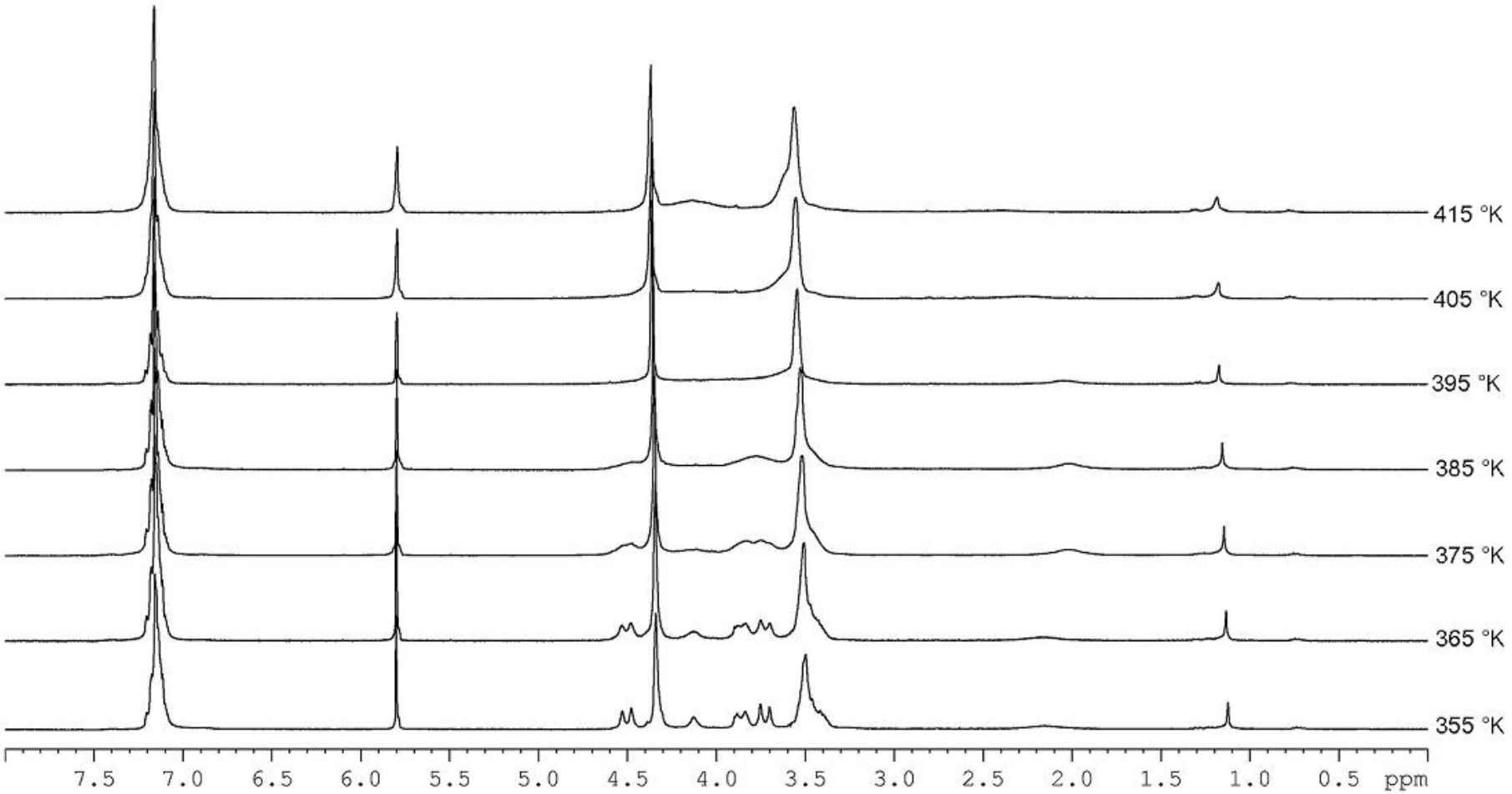


Figure S4. Evaluation of the coalescence temperature for **1** (300 MHz, $C_2D_2Cl_4$)

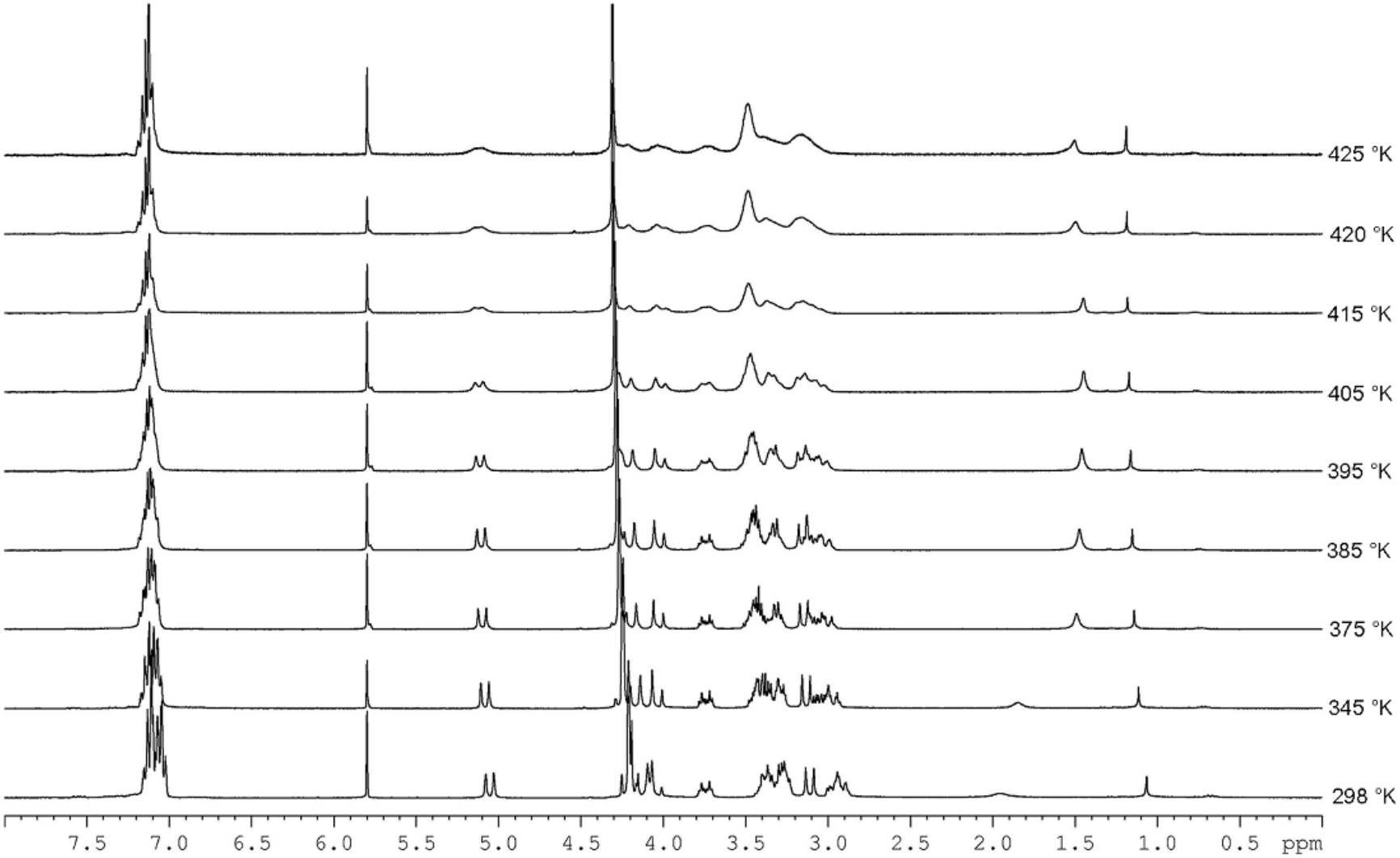


Figure S5. Variable temperature ^{1}H-NMR spectra of **2** (300 MHz, $C_2D_2Cl_4$)

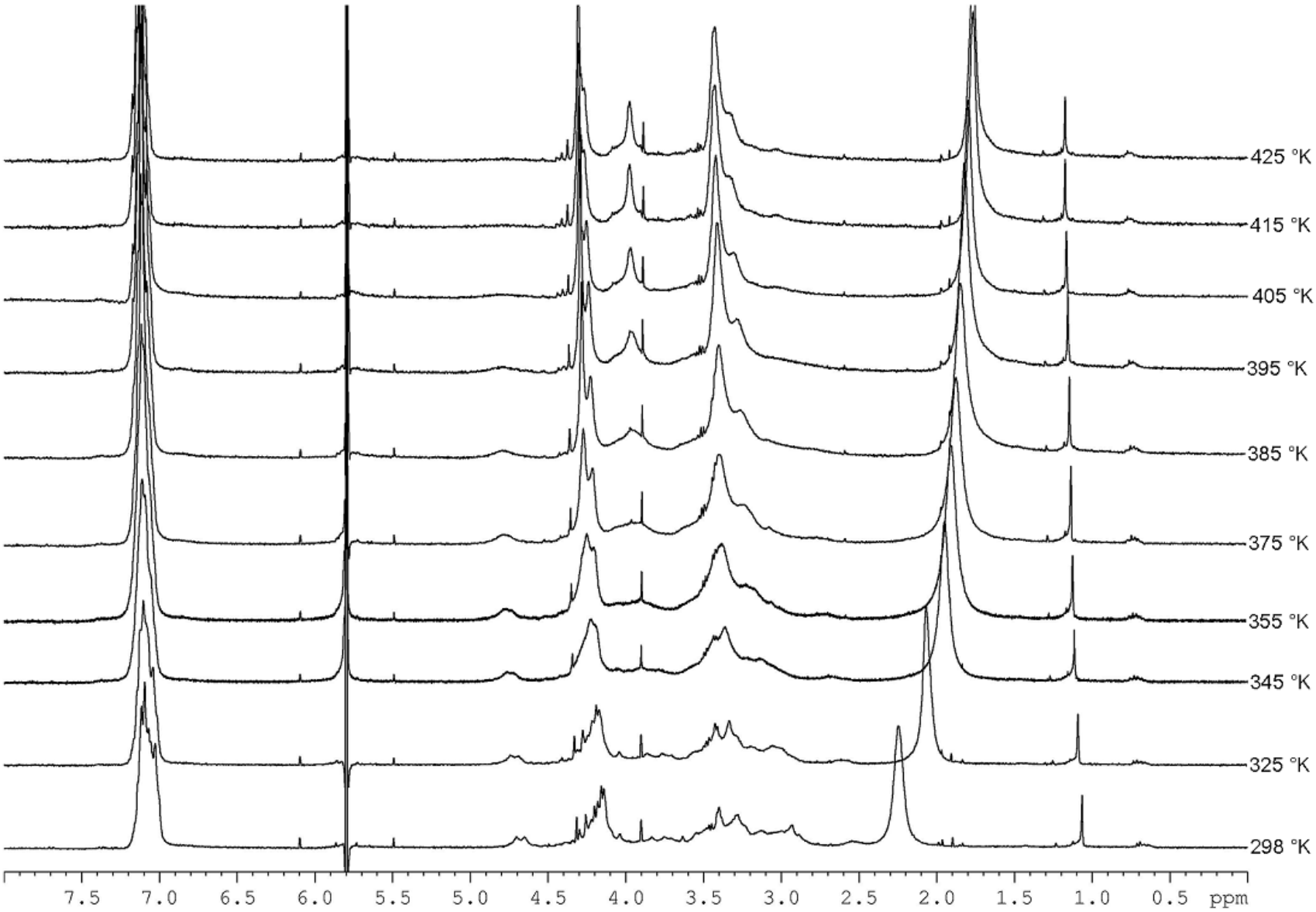


Figure S6. Variable temperature ^{1}H-NMR spectra of **3** (300 MHz, $C_2D_2Cl_4$)

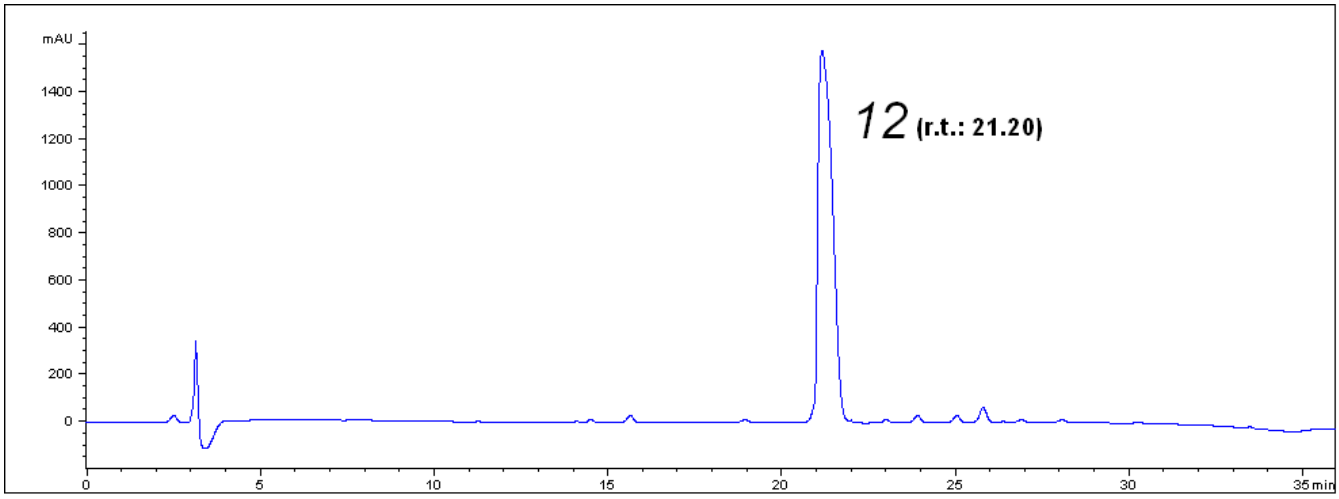
3.0 HPLC analysis

3.1 HPLC chromatograms for linear peptoids 12, 15, 17

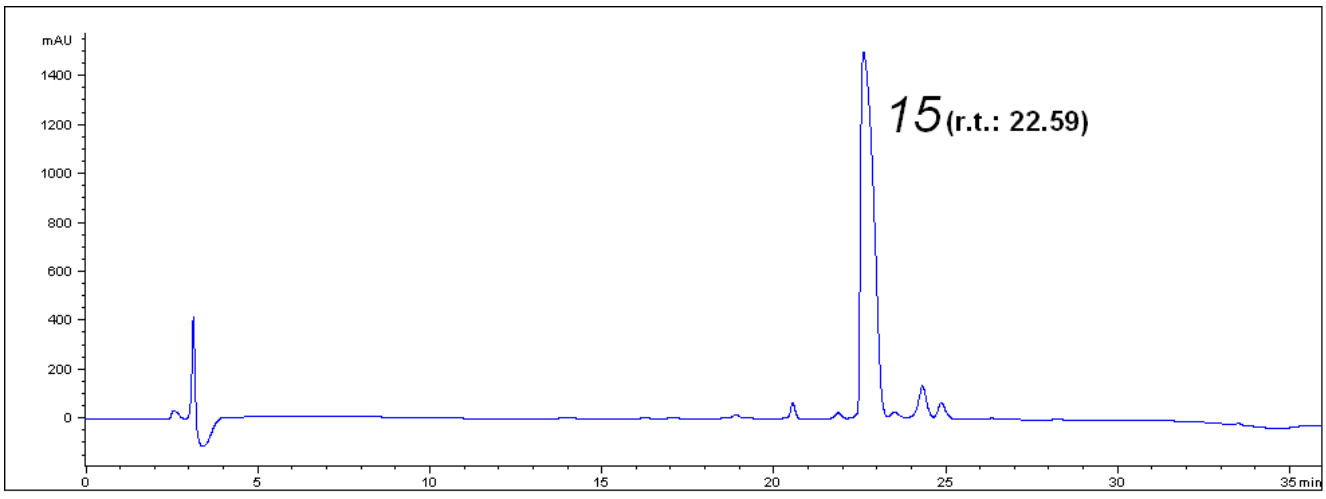
HPLC analysis for linear peptoids **12**, **15**, and **17** (from solid-phase synthesis).

Conditions: 5 → 100% B in 30 minutes (A: 0.1% TFA in water, B: 0.1% TFA in acetonitrile), flow: 1.0 ml/min, 220 nm. C_{18} reversed-phase analytical column (Waters, µBondapak, 10 µm, 125Å, 3.9 mm × 300 mm)

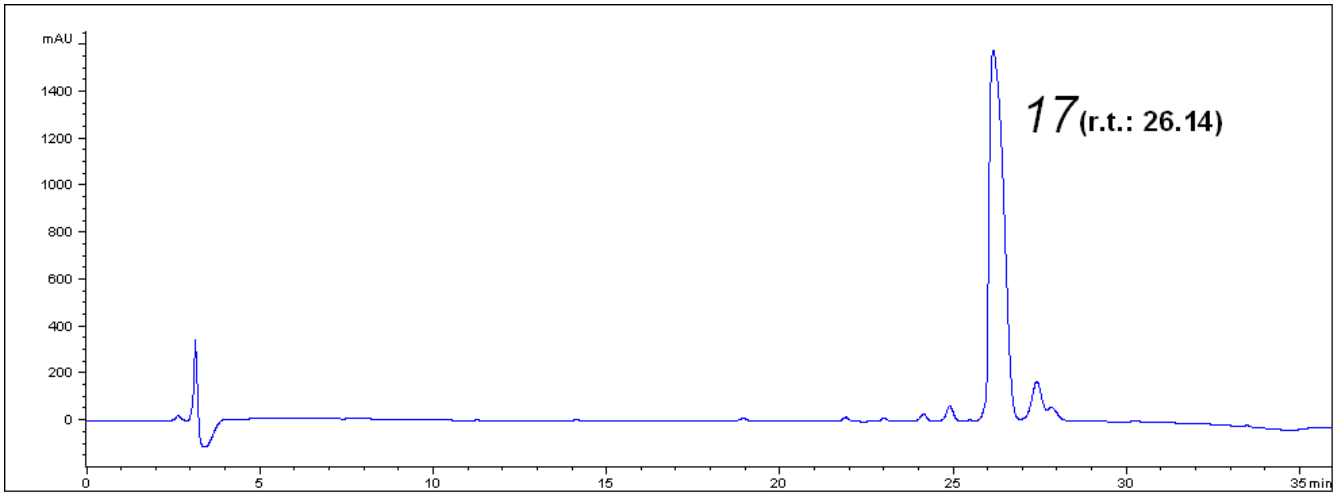
Compound 12



Compound 15



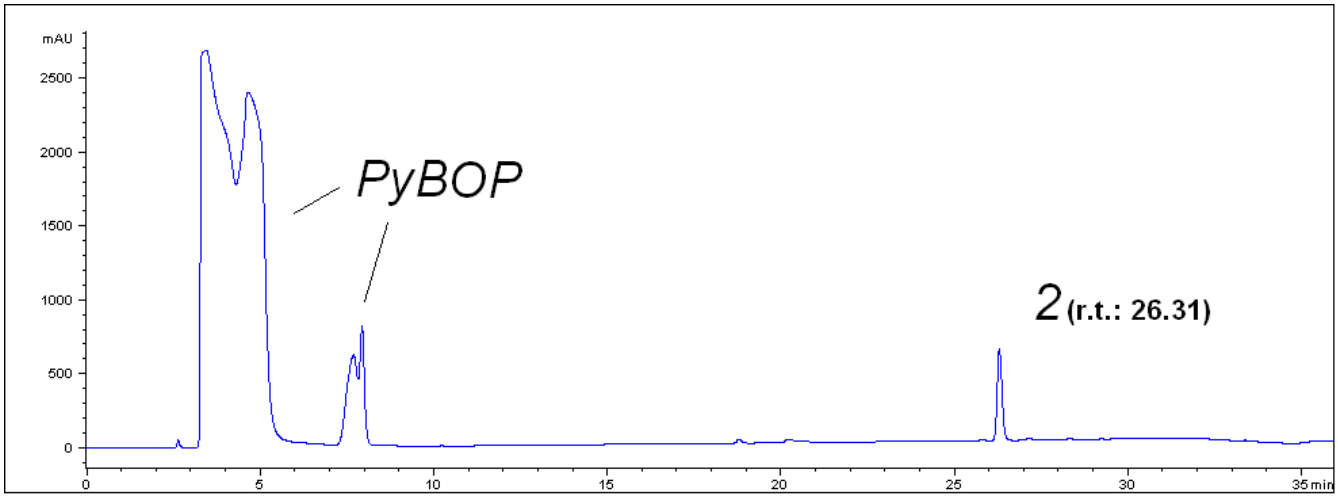
Compound 17

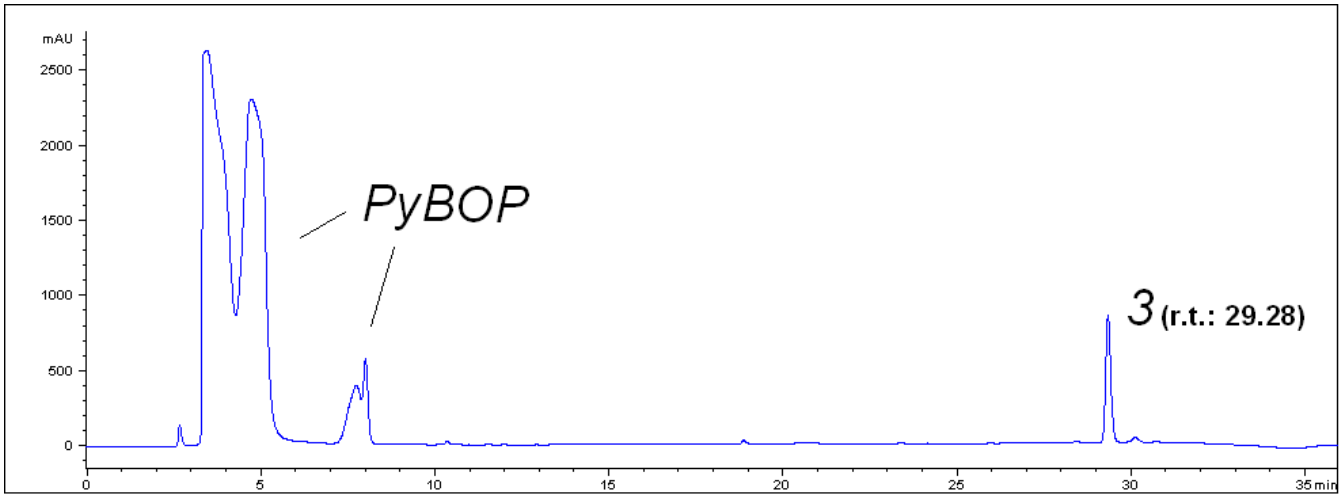


3.2 HPLC chromatograms for cyclization of peptoids 15 and 17

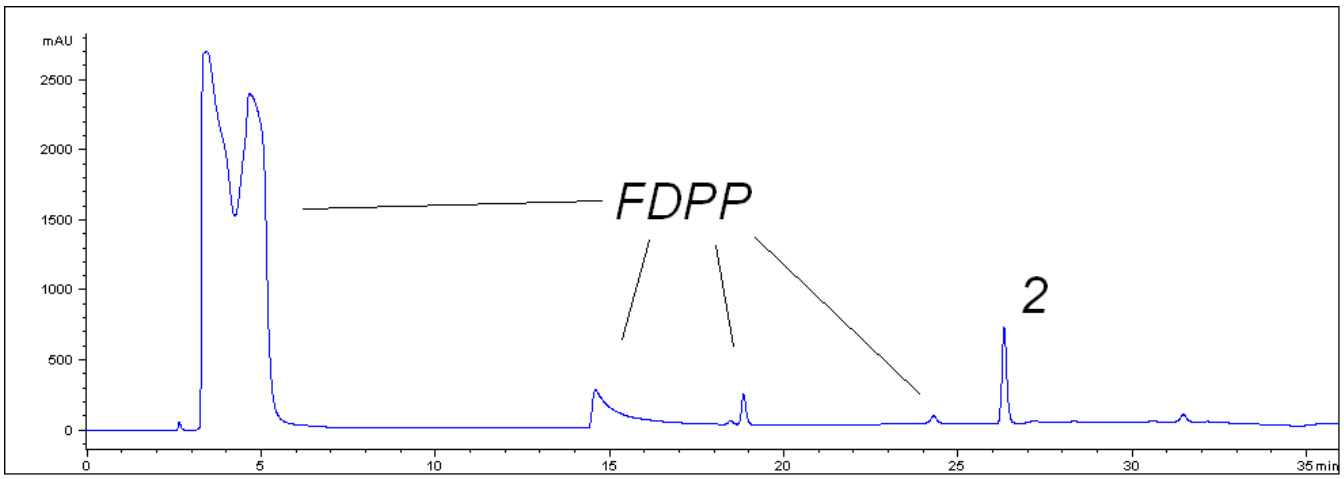
Conditions: 5 → 100% B in 30 minutes (A: 0.1% TFA in water, B: 0.1% TFA in acetonitrile), flow: 1.0 ml/min, 220 nm. C_{18} reversed-phase analytical column (Waters, μBondapak, 10 μm, 125Å, 3.9 mm × 300 mm).

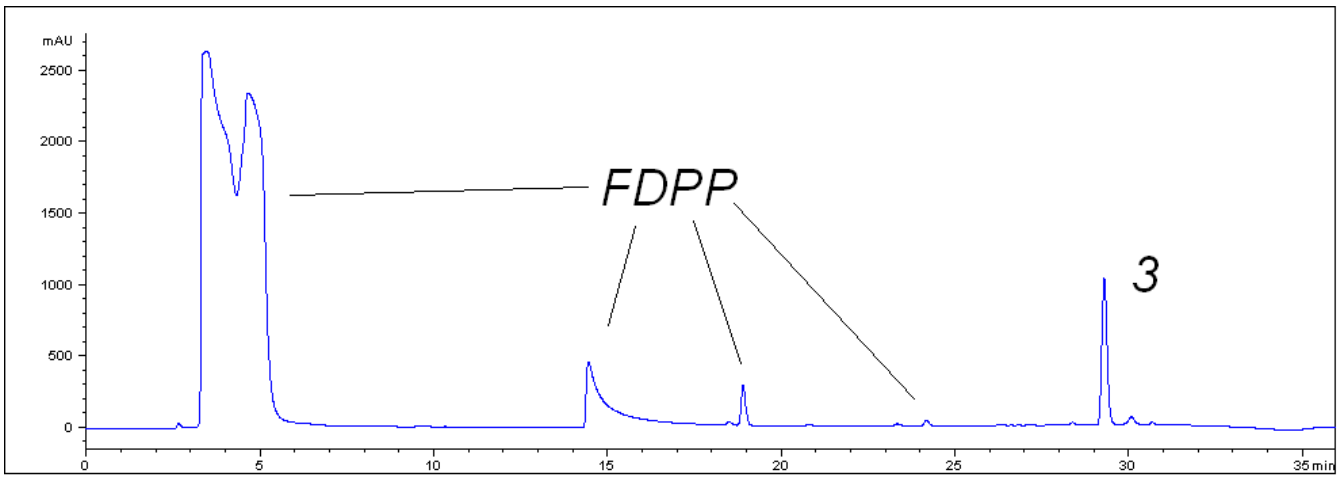
PyBOP cyclization (10 μL of the reaction mixture reaction were quenched, after 18 hours, with 140 μL of 1:1 mixture H_2O/CH_3CN and injected in the HPLC)



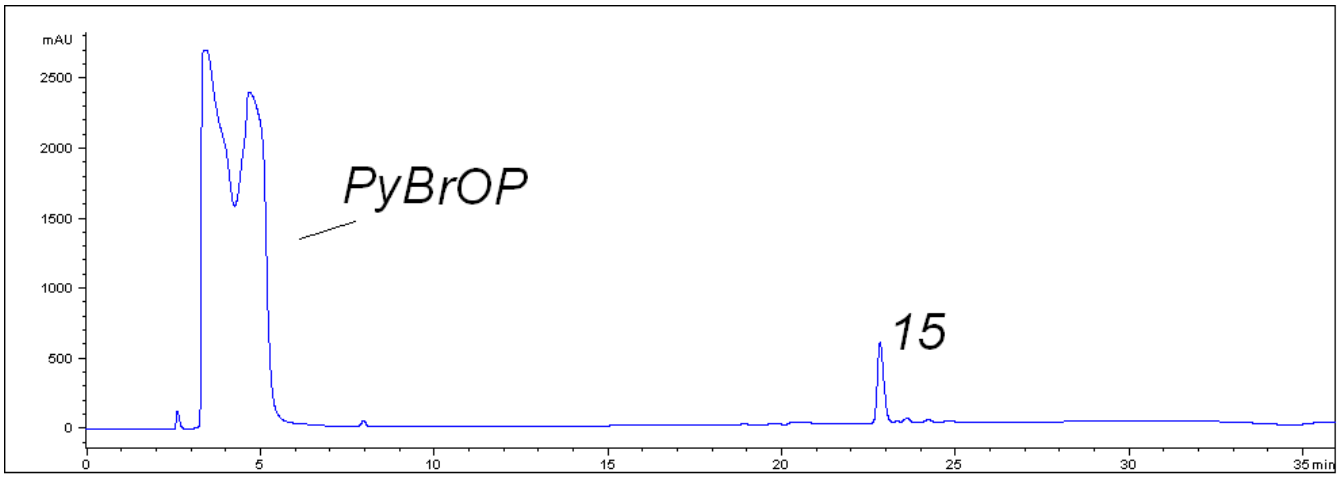


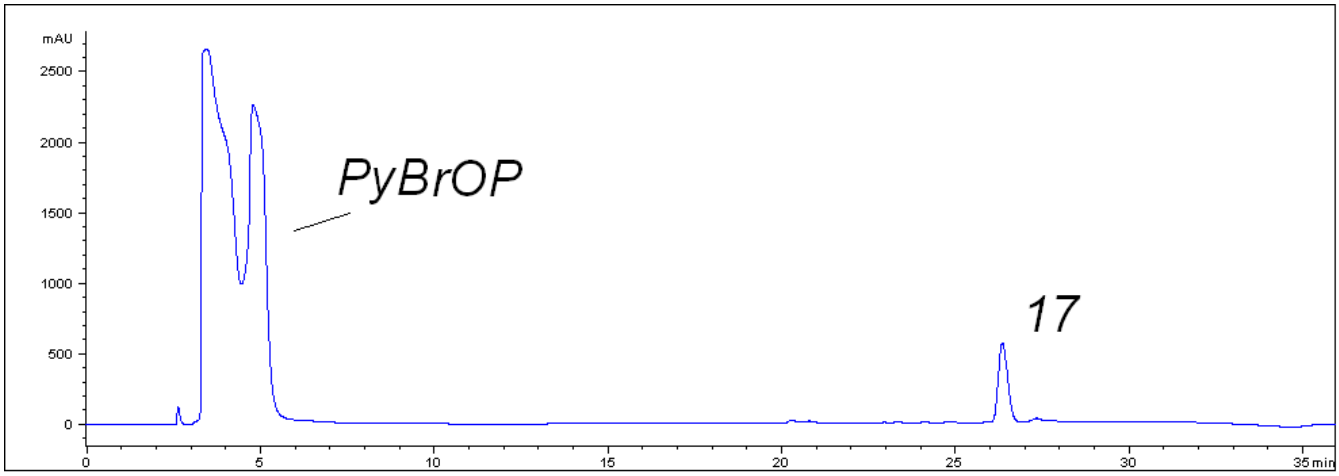
FDPP cyclization (10 μL of the reaction mixture reaction were quenched, after 18 hours, with 140 μL of 1:1 mixture H_2O/CH_3CN and injected in the HPLC)





Attempted PyBrOP cyclization (10 μL of the reaction mixture reaction were quenched, after 72 hours, with 140 μL of 1:1 mixture H_2O/CH_3CN and injected in the HPLC)


mAU
2500
2000
1500
1000
500
0
PyBrOP
15
0
5
10
15
20
25
30
35 min


mAU
2500
2000
1500
1000
500
0
PyBrOP
17
0
5
10
15
20
25
30
35 min

4.0 Complexation studies

4.1 Synthesis of the complexes

To a 4.0 mM solution of **3** in CD_3CN:$CDCl_3$ 9:1 (0.5 mL), were added increasing amounts of picrates. After any addition the mixture was stirred vigorously for 15 minutes and the spectrum was acquired.

Compex sodium picrate-3 (Figure 3 (c) of the paper)

^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution, spectra of the 1.5:1 complex) δ: 3.28 (6H, m, -NC*H*HCH$_2$OBn); 3.48-3.60 (18H, m, -NCH*H*C*H*$_2$OBn); 3.83 (6H, d, *J* = 16.8 Hz, -OCC*H*HN, pseudoequatorial); 4.41 (6H, d, *J* = 12.0 Hz, -OC*H*HAr); 4.48 (6H, d, *J* = 12.0 Hz, -OCH*H*Ar); 4.62 (6H, d, *J* = 16.8 Hz, -OCCH*H*N, pseudoaxial); 7.28-7.37 (30H, m, Ar-H).

^{13}C NMR (100 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution) δ: 49.9 (× 6), 50.9 (× 6), 69.1 (× 6), 73.8 (× 6), 126.7 (× 2, *C*-H; picrate), 127.6 (× 2, *o*-position; picrate), 128.6 (× 18), 129.3 (× 12), 139.4 (× 6), 142.6 (× 1, *p*-position; picrate), 161.2 (× 1, *ipso*-position; picrate), 170.9 (× 6).

ESMS: 1169.6 m/z [M+Na$^+$].

Compex ammonium picrate-3 (Figure 5 (a) of the paper, see also Figure S8)

^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution, spectra of the 4:1 complex) δ: 3.32 (6H, m, -NC*H*HCH$_2$OBn); 3.46-3.60 (18H, m, -OCC*H*HN, pseudoequatorial and -NCH$_2$C*H*$_2$OBn, overlapped); 3.70 (6H, m, -NCH*H*CH$_2$OBn); 4.45 (6H, d, *J* = 12.0 Hz, -OC*H*HAr); 4.51 (6H, d, *J* = 12.0 Hz, -OCH*H*Ar); 4.71 (6H, d, *J* = 16.8 Hz, -OCCH*H*N, pseudoaxial); 7.28-7.37 (30H, m, Ar-H).

^{13}C NMR (100 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution) δ: 49.3 (× 6), 50.1 (× 6), 68.8 (× 6), 73.8 (× 6), 126.6 (× 2, *C*-H; picrate), 127.6 (× 2, *o*-position; picrate), 128.6 (× 18), 129.4 (× 12), 139.3 (× 6), 142.9 (× 1, *p*-position; picrate), 162.0 (× 1, *ipso*-position [phenolic]; picrate), 170.7 (× 6).

ESMS: 1147.6 m/z [M+H$^+$].

Compex benzylammonium picrate-3 (Figure 5 (b) of the paper, see also Figure S9)

^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution, spectra of the 4:1 complex) δ: 3.13 (6H, m, -NC*H*HCH$_2$OBn); 3.39-3.59 (24H, m, -NCH*H*CH$_2$OBn, -NCH$_2$C*H*$_2$OBn and -OCC*H*HN pseudoequatorial, overlapped); 4.13 (2H, bs, ArC*H*$_2$NH$_3^+$); 4.44 (6H, d, *J* = 12.0 Hz, -OC*H*HAr); 4.48 (6H, d, *J* = 12.0 Hz, -OCH*H*Ar); 4.60 (6H, d, *J* = 16.8 Hz, -OCCH*H*N, pseudoaxial); 7.28-7.61 (35H, m, Ar-H).

^{13}C NMR (100 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution) δ: 44.5 (× 1, Bn-*C*H_2-NH_4^+), 49.2 (× 6), 50.0 (× 6), 69.0 (× 6), 73.8 (× 6), 126.6 (× 2, *C*-H; picrate), 127.6 (× 2, *o*-position; picrate), 128.6 (× 12), 128.7 (× 6), 128.7 (× 2, benzylammonium), 129.4 (× 12), 130.0 (× 2, benzylammonium), 130.1 (× 1, benzylammonium), 134.1 (× 1, benzylammonium), 139.3 (× 6), 142.9 (× 1, *p*-position; picrate), 162.1 (× 1, *ipso*-position [phenolic]; picrate), 170.7 (× 6).

ESMS: 1147.6 m/z [M+H^+], 1254.6 [M+$BnNH_3^+$], see Figure S7.

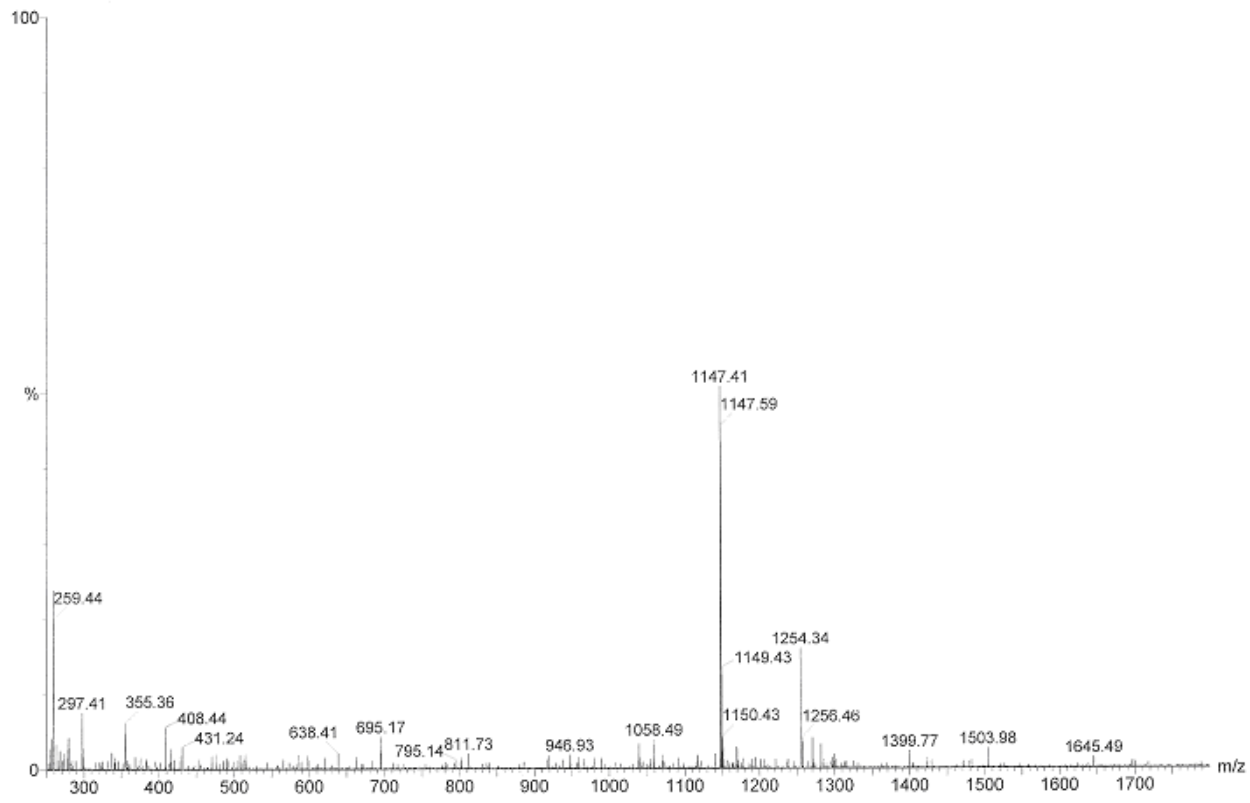


Figure S7. Benzylammonium picrate-**3** complex: ESI MS spectrum (complex dissolved in 1:1 MeOH/H_2O, no formic acid added)

4.2 ^{1}H-NMR spectra of complexes and variable temperature experiments

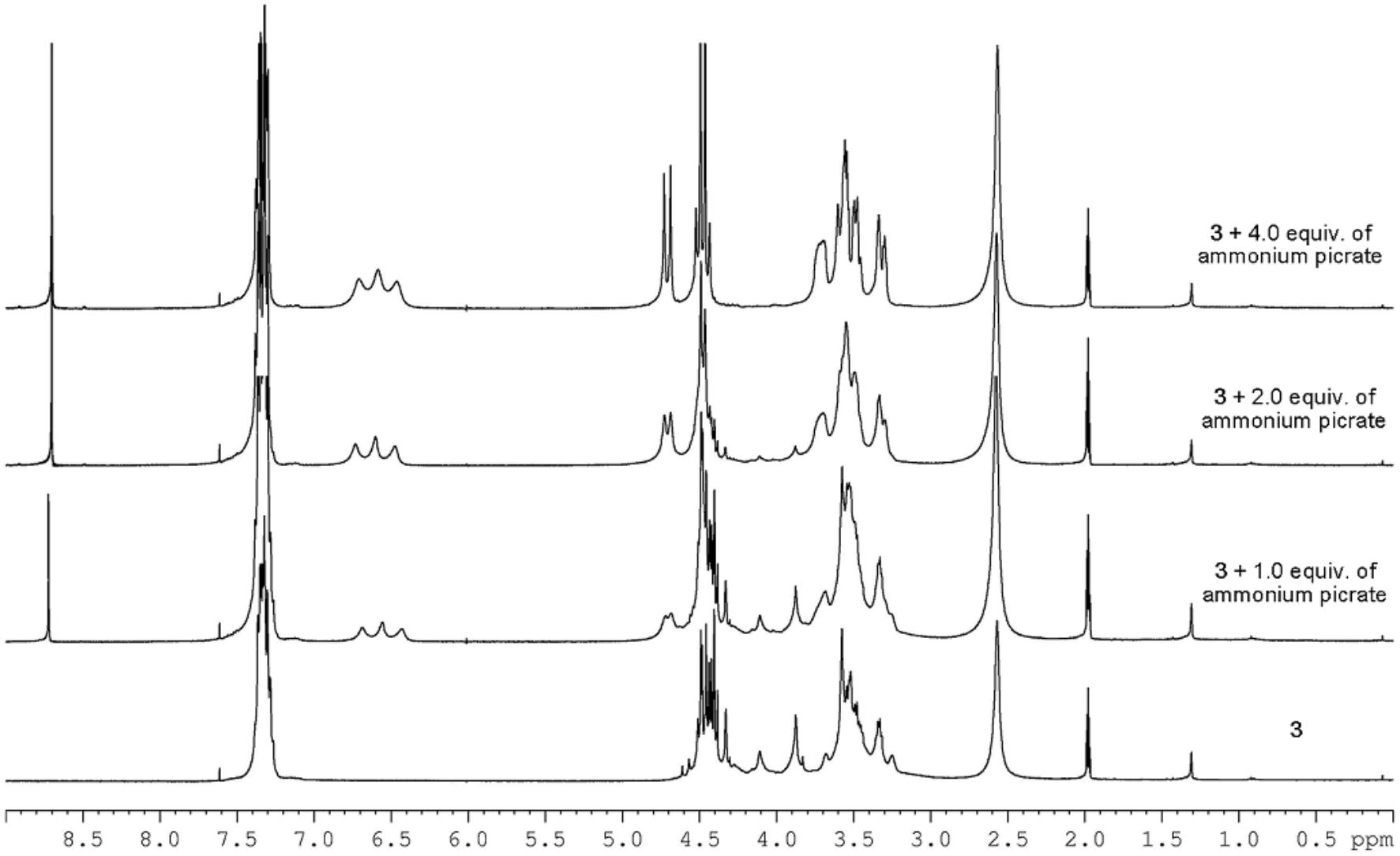


Figure S8. Complexation of **3** with ammonium picrate. ^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution)

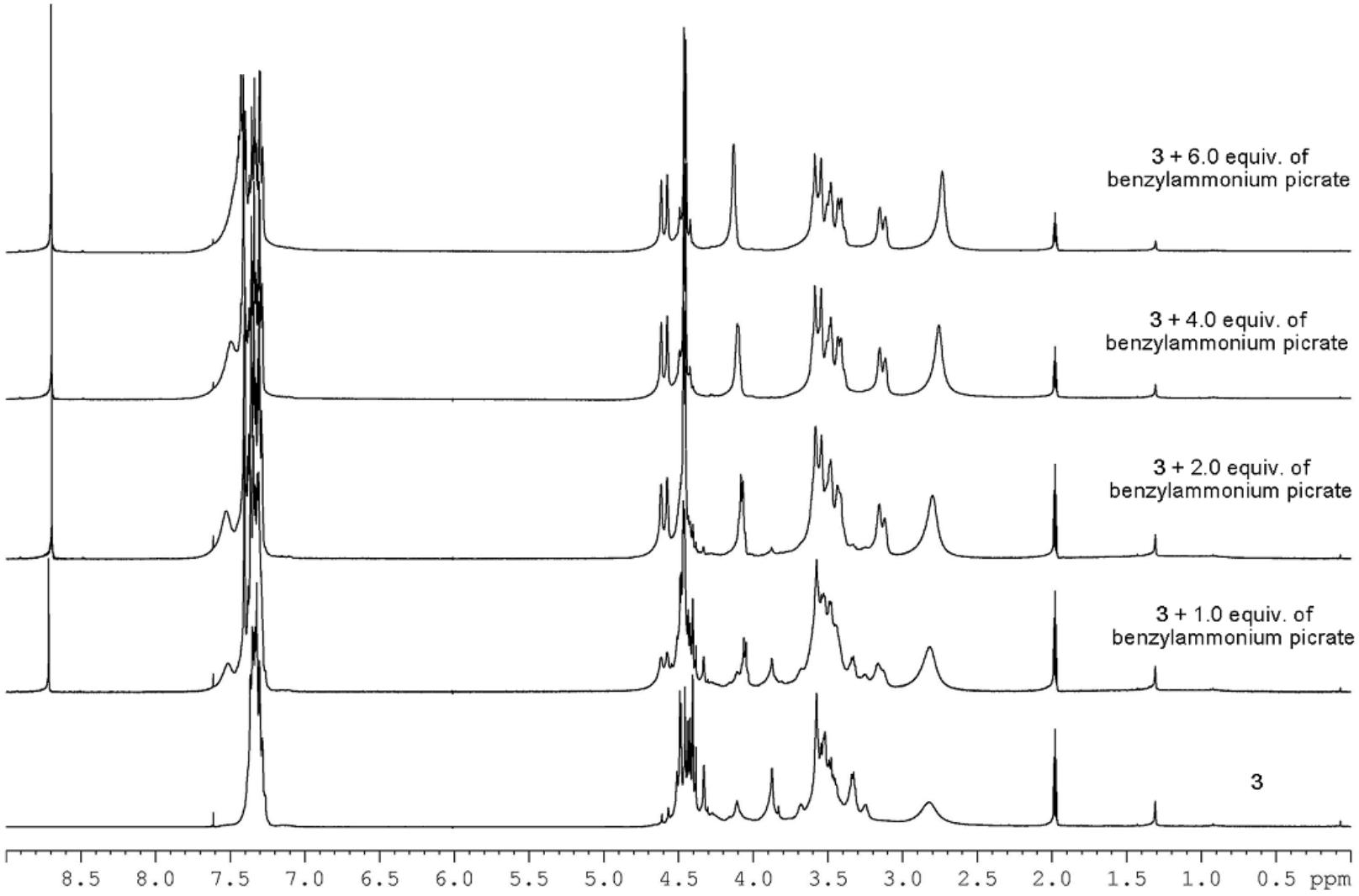


Figure S9. Complexation of **3** with benzylammonium picrate. ^{1}H NMR (400 MHz, CD_3CN:$CDCl_3$ 9:1, 25 °C, 4.0 mM solution)

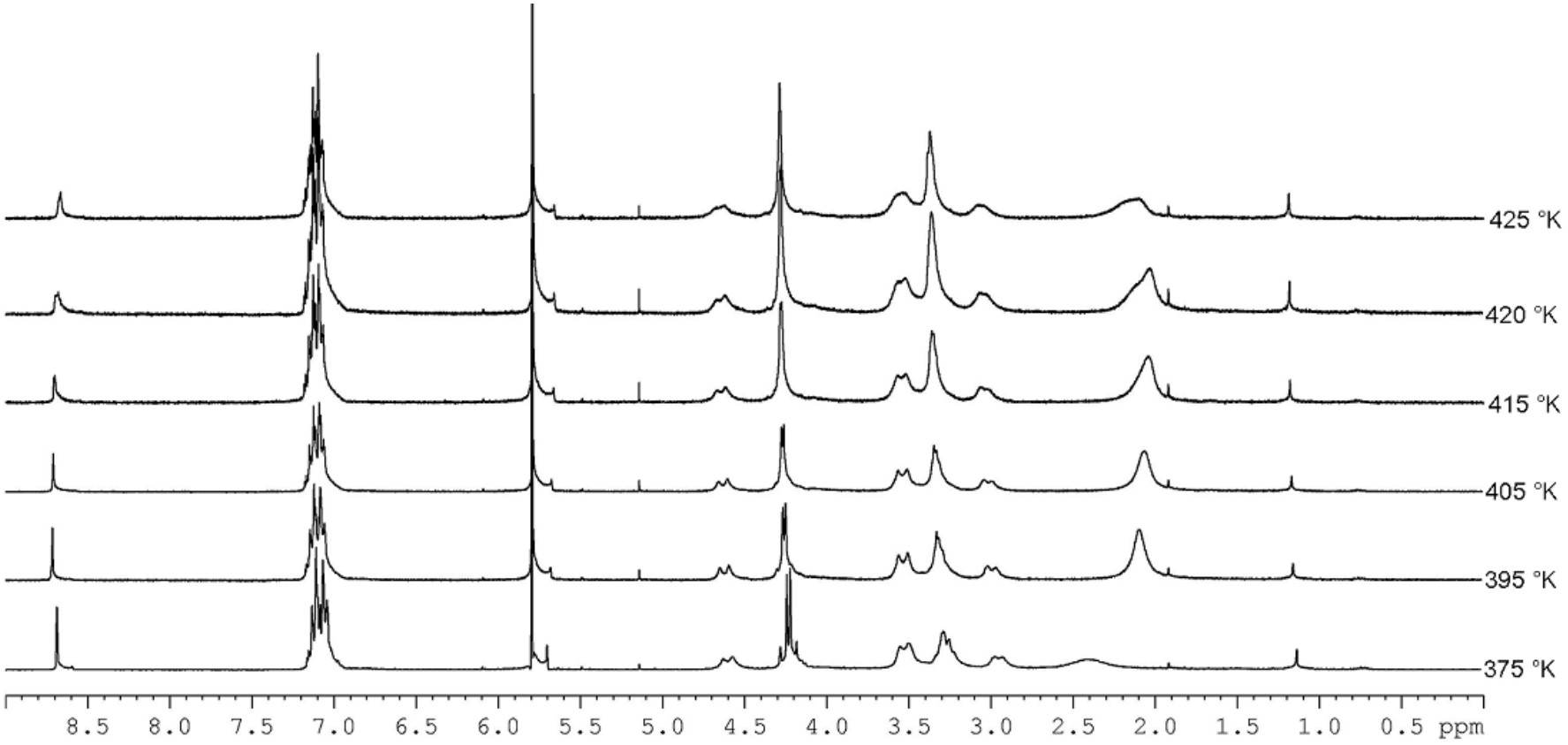


Figure S9. Variable temperature ^{1}H-NMR spectra of the complex between **3** and sodium picrate (mixed in a 1:1.5 ratio) (300 MHz, $C_2D_2Cl_4$)

5.0 Computational details

In order to allow a full exploration of the conformational space of the molecules, MM/MD calculations at different temperatures (300 K, 500K, 700K/10 ns) were performed using the AMBER force field (MacroModel software package) All the so obtained structures (in number of 100) were minimized using the Polak-Ribier Conjugate Gradient algorithm (PRCG, 1000 steps, maximum derivative less than 0.05 kcal/mol). This led to the selection of the lowest energy minimum conformer for the molecules; a parallel analysis was performed using the MonteCarlo Multiple Minimum (MCMM) method (50K steps) of the MacroModel package,[1] leading to the same results obtained by MM/MD calculations. The initial geometries of the minimum energy conformers were further optimized at the DFT MPW1PW91[2] level using the 6-31G(d) basis set (Gaussian 03 Software Package).[3] GIAO[4] ^{1}H and ^{13}C calculations were performed using the MPW1PW91 functional and the 6-31G(d,p) basis set, using as input the geometry previously optimized at MPW1PW91/6-31G(d) level.

5.1 Cartesian coordinates of the considered structures, optimized at MPW1PW91/6-31G(d) DFT level

Compound **1**

Energy = -1896.1408546 A.U.

Atom	X	Y	Z
C	-1.696252	1.029239	-1.311232
C	-1.704946	-0.257407	-0.480386
N	-0.605725	1.845036	-1.278585
C	0.597105	1.636673	-0.484900
C	1.701412	0.985690	-1.323322
N	1.867870	-0.365952	-1.285019
C	1.087340	-1.302504	-0.488270
C	-0.032146	-1.931744	-1.323156
N	-1.284893	-1.397822	-1.282937
O	2.388460	1.698765	-2.045949
O	0.238989	-2.882403	-2.048155
O	-2.661655	1.273618	-2.026242
C	2.862124	-0.949242	-2.183764
C	4.243961	-1.009690	-1.563422
C	-0.603369	3.002675	-2.170804
C	-1.251320	4.221095	-1.543705
C	-2.288623	-1.965798	-2.180999
C	-3.017884	-3.145031	-1.568084
O	-0.474338	4.625812	-0.433847
O	4.198378	-1.872828	-0.444030
O	-3.738056	-2.693042	-0.437668
C	5.449954	-2.059978	0.175212
C	-4.506180	-3.699215	0.180023
C	-0.973258	5.776363	0.211406
C	6.916390	1.343868	2.379259
C	7.799664	0.546627	1.658326
C	7.322057	-0.539129	0.929183

C	5.962425	-0.848727	0.921907
C	5.082769	-0.043197	1.648044
C	5.555106	1.047780	2.368821
C	-4.616010	5.139307	2.428841
C	-3.576838	4.213469	2.500467
C	-2.408211	4.419058	1.777027
C	-2.262495	5.548531	0.967662
C	-3.311016	6.464325	0.894640
C	-4.480432	6.266085	1.624896
C	-2.233078	-6.644008	2.361023
C	-1.809838	-5.317392	2.323477
C	-2.537019	-4.371778	1.609133
C	-3.692056	-4.739784	0.916536
C	-4.102586	-6.072124	0.949783
C	-3.382593	-7.019338	1.672841
H	-2.740978	-0.427438	-0.187534
H	-1.118871	-0.200758	0.434407
H	0.359071	1.101222	0.431765
H	0.970523	2.618826	-0.194873
H	1.751197	-2.117482	-0.200010
H	0.746834	-0.827807	0.429543
H	2.906388	-0.335205	-3.084671
H	2.517999	-1.950162	-2.451782
H	4.570068	-0.004070	-1.271530
H	-1.155260	2.736037	-3.073537
H	0.434261	3.212813	-2.437726
H	-2.278369	3.984553	-1.240253
H	-1.782527	-2.297904	-3.088901
H	-2.991142	-1.170052	-2.436427
H	-2.300941	-3.927307	-1.290921
H	4.956314	-1.395708	-2.309680
H	-1.294779	5.030150	-2.290225
H	-3.710815	-3.566361	-2.313507
H	5.301071	-2.891660	0.872345
H	6.198491	-2.384645	-0.564154
H	-5.157031	-3.169479	0.884095
H	-5.158067	-4.191903	-0.558067
H	-0.180817	6.078409	0.904171
H	-1.105815	6.595011	-0.512707
H	7.285081	2.195314	2.942325
H	8.860772	0.775427	1.653828
H	8.014836	-1.152001	0.358049
H	4.022306	-0.274310	1.630472
H	4.860412	1.670087	2.924543
H	-5.528538	4.979194	2.994186
H	-3.679332	3.330386	3.123651
H	-1.598711	3.697228	1.824812
H	-3.213082	7.341170	0.259716
H	-5.288489	6.987658	1.557027
H	-1.665624	-7.382150	2.918758
H	-0.909809	-5.019916	2.852786
H	-2.208612	-3.337937	1.570495
H	-4.993581	-6.372858	0.404393
H	-3.714360	-8.052787	1.689246

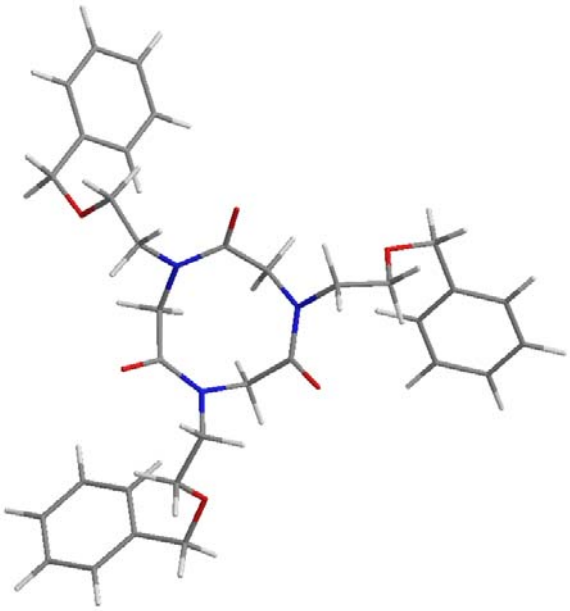


Figure S10. Structure of **1** from computational studies.

Compound **2**

Energy= -2528.204048 A.U.

Atom	X	Y	Z
C	1.386751	-0.301402	0.299342
N	1.362122	-1.080110	-0.820677
C	0.786560	-2.411178	-0.735816
C	-0.449645	-2.573164	-1.633936
C	1.775961	1.164031	0.086127
N	-1.623597	-1.982292	-1.264084
C	-1.776128	-1.164124	-0.086019
C	-1.386892	0.301323	-0.299114
N	-1.362146	1.079881	0.820997
C	-0.786649	2.410989	0.736240
C	0.449650	2.572974	1.634238
N	1.623596	1.982203	1.264196
O	-1.044768	0.730401	-1.397631
O	0.342225	3.232863	2.662796
O	1.044753	-0.730398	1.397930
O	-0.342081	-3.232953	-2.662542
C	-1.812350	0.670240	2.146883
C	-3.288834	0.917900	2.412739
C	-2.780096	-2.180401	-2.126812
C	-3.163125	-0.969095	-2.956435
C	2.780248	2.180451	2.126690
C	3.163474	0.969268	2.956411
C	1.812380	-0.670629	-2.146585
C	3.288888	-0.918336	-2.412316
O	3.840146	0.036817	2.139440
O	-4.051578	-0.120693	1.847496
O	4.051554	0.120474	-1.847389
O	-3.839969	-0.036750	-2.139483
C	3.972789	-1.221695	2.772210
C	-5.443137	0.085222	2.009762
C	5.443139	-0.085460	-2.009440

C	-3.972467	1.221840	-2.772126
C	7.592972	3.320099	-0.495909
C	7.660204	3.000044	-1.847584
C	6.959160	1.900565	-2.337519
C	6.192722	1.107272	-1.485085
C	6.131202	1.432872	-0.126709
C	6.824799	2.534872	0.362011
C	6.184166	-3.882549	0.210896
C	6.832868	-2.830916	0.855918
C	6.116652	-1.976039	1.687132
C	4.744605	-2.154058	1.880571
C	4.104763	-3.208716	1.229364
C	4.818328	-4.071743	0.400838
C	-7.593343	-3.319519	0.494912
C	-6.825177	-2.533978	-0.362729
C	-6.131448	-1.432250	0.126415
C	-6.192829	-1.107237	1.484937
C	-6.959258	-1.900844	2.337088
C	-7.660431	-3.000053	1.846732
C	-6.184209	3.882512	-0.210937
C	-4.818349	4.071738	-0.400691
C	-4.104658	3.208765	-1.229165
C	-4.744398	2.154134	-1.880515
C	-6.116469	1.976086	-1.687268
C	-6.832809	2.830904	-0.856101
H	0.581195	-2.613165	0.315580
H	1.497613	-3.155445	-1.103681
H	1.155277	1.558883	-0.721548
H	2.811725	1.210930	-0.256683
H	-1.155622	-1.559014	0.721771
H	-2.811954	-1.211005	0.256608
H	-0.581395	2.613117	-0.315152
H	-1.497700	3.155188	1.104249
H	-1.230563	1.243633	2.872205
H	-1.578811	-0.379917	2.326284
H	-3.451959	0.952431	3.502284
H	-3.632841	-2.476937	-1.506141
H	-2.528327	-3.004831	-2.794178
H	-3.818518	-1.286178	-3.784168
H	2.528597	3.004978	2.793977
H	3.632879	2.476902	1.505822
H	2.259728	0.519082	3.384152
H	3.819049	1.286475	3.783951
H	1.578877	0.379508	-2.326117
H	1.230602	-1.244094	-2.871859
H	3.592031	-1.893186	-2.000884
H	3.452080	-0.953242	-3.501841
H	-2.259271	-0.518864	-3.383900
H	-3.591967	1.892897	2.001658
H	4.498036	-1.097532	3.733194
H	2.976565	-1.631197	2.982465
H	-5.676513	0.236825	3.074988
H	-5.743202	0.997662	1.472779
H	5.743196	-0.997642	-1.472016
H	5.676607	-0.237539	-3.074576
H	-2.976196	1.631339	-2.982180
H	-4.497561	1.097806	-3.733210
H	8.136687	4.177177	-0.110925
H	8.254317	3.607342	-2.523276
H	7.007826	1.657453	-3.395528

H	5.532116	0.824099	0.544060
H	6.771760	2.779205	1.418826
H	6.743693	-4.555301	-0.431477
H	7.898978	-2.681690	0.716490
H	6.625127	-1.159458	2.191389
H	3.038925	-3.353014	1.378238
H	4.308498	-4.893521	-0.092610
H	-8.137165	-4.176381	0.109597
H	-6.772248	-2.777854	-1.419655
H	-5.532349	-0.823249	-0.544136
H	-7.007814	-1.658191	3.395208
H	-8.254534	-3.607598	2.522211
H	-6.743830	4.555224	0.431394
H	-4.308600	4.893496	0.092873
H	-3.038800	3.353082	-1.377876
H	-6.624862	1.159521	-2.191634
H	-7.898936	2.681655	-0.716828

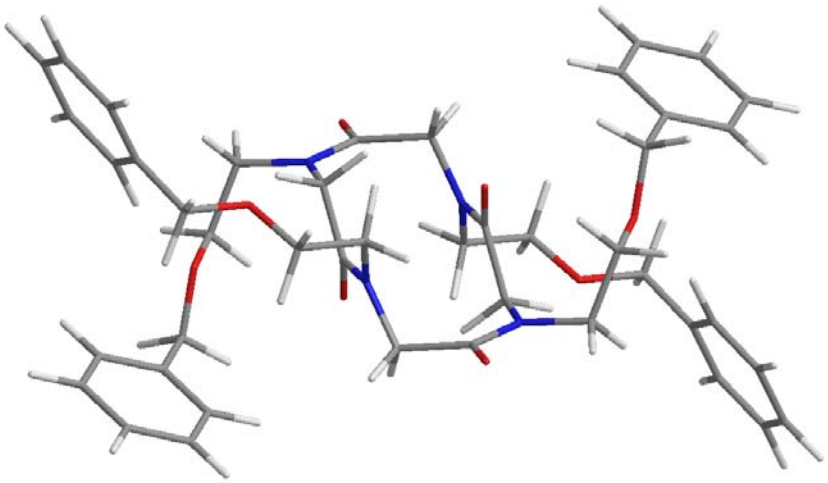


Figure S11. Structure of **2** from computational studies.

Compound **2** (*ccct* conformer)
Energy -2528.198994 A.U.

Atom	X	Y	Z
C	1.238603	0.839463	-0.453069
N	0.635230	1.575764	0.523585
C	0.666946	1.294998	1.944935
C	-0.658790	1.088366	2.697381
C	2.104237	-0.360757	-0.041048
N	-1.767021	0.543991	2.100452
C	-1.795803	-0.042233	0.775270
C	-0.819670	-1.206219	0.636456
N	-0.499493	-1.630283	-0.622878
C	0.496209	-2.680406	-0.759497
C	1.733086	-2.277513	-1.568859
N	2.441103	-1.181238	-1.178630
O	-0.295601	-1.694758	1.632581
O	2.061386	-2.954832	-2.534869
O	1.128302	1.142911	-1.636044
O	-0.653481	1.424802	3.873231
C	-1.111995	-1.164927	-1.858822

C	-2.196050	-2.080286	-2.396978
C	-2.909258	0.277833	2.967093
C	-4.192348	0.952033	2.517582
C	3.558354	-0.765431	-2.013960
C	4.873738	-1.392394	-1.596096
C	0.005635	2.829411	0.119653
C	1.010714	3.938689	-0.129077
O	-3.317874	-2.025363	-1.548108
O	5.253531	-0.876369	-0.331360
O	1.700010	4.199570	1.075239
O	-4.765137	0.198300	1.468217
C	-4.350314	-2.890191	-1.981707
C	-5.502759	-2.851644	-1.018013
C	6.420497	-1.479559	0.188212
C	6.223648	-2.906001	0.647646
C	2.741952	5.138838	0.933989
C	3.928725	4.626643	0.148040
C	-5.858927	0.831563	0.831409
C	-5.427538	1.923230	-0.118657
C	-6.807027	-2.673474	-1.479527
C	-7.881149	-2.685435	-0.592939
C	-7.656214	-2.865128	0.768430
C	-6.354879	-3.032761	1.237922
C	-5.285771	-3.030720	0.350004
C	7.188689	-3.879025	0.390862
C	7.027520	-5.180535	0.859360
C	5.889232	-5.524155	1.581262
C	4.914918	-4.560506	1.833542
C	5.082981	-3.260168	1.372080
C	4.318104	3.290040	0.253515
C	5.420212	2.812521	-0.447863
C	6.158568	3.676763	-1.253845
C	5.783347	5.012632	-1.359333
C	4.668505	5.481060	-0.668862
C	-4.674008	1.593875	-1.250868
C	-4.248298	2.584995	-2.127649
C	-4.572018	3.920087	-1.886934
C	-5.323113	4.256581	-0.766234
C	-5.745825	3.260829	0.112534
H	1.142229	2.127974	2.466801
H	1.262815	0.404109	2.141699
H	1.629149	-0.969370	0.728998
H	3.037907	0.012123	0.392435
H	-1.609755	0.719306	0.017829
H	-2.810741	-0.402904	0.594432
H	0.081554	-3.541694	-1.288522
H	0.769496	-3.000845	0.247887
H	-0.322609	-1.062670	-2.609305
H	-1.526111	-0.167706	-1.719053
H	-1.828894	-3.114368	-2.483008
H	-2.462388	-1.746485	-3.412389
H	-2.631695	0.639773	3.956512
H	-3.074061	-0.804099	3.031894
H	-3.980118	1.981862	2.199463
H	-4.897047	0.997491	3.363123
H	3.622345	0.324184	-1.980992
H	3.339323	-1.065808	-3.039903
H	5.647051	-1.153467	-2.343152
H	4.766466	-2.482751	-1.554300
H	-0.688387	3.124584	0.910561

H	-0.563481	2.665198	-0.798601
H	0.476890	4.841164	-0.467443
H	1.702748	3.635779	-0.923250
H	-3.953729	-3.916037	-2.057225
H	-4.688527	-2.603003	-2.988881
H	6.713128	-0.850376	1.035316
H	7.235095	-1.434177	-0.550752
H	3.045632	5.381361	1.957844
H	2.364695	6.067187	0.477445
H	-6.555746	1.232881	1.582367
H	-6.372710	0.033041	0.289907
H	-6.985141	-2.524901	-2.541142
H	-8.891113	-2.548830	-0.966386
H	-8.490748	-2.871927	1.462444
H	-6.172521	-3.164711	2.299440
H	-4.272188	-3.154495	0.716220
H	8.075048	-3.617423	-0.181543
H	7.787319	-5.927366	0.651388
H	5.758280	-6.539137	1.942658
H	4.022801	-4.823123	2.393542
H	4.323850	-2.508823	1.565329
H	3.738546	2.623656	0.884421
H	5.689851	1.763509	-0.371606
H	7.019913	3.308439	-1.802273
H	6.350381	5.689477	-1.990935
H	4.369510	6.521527	-0.769056
H	-4.424319	0.552398	-1.436731
H	-3.669777	2.318670	-3.007298
H	-4.241990	4.692677	-2.574300
H	-5.579206	5.293523	-0.572578
H	-6.332831	3.527007	0.987842

Compound **2** (*cccc* conformer)
Energy -2528.190639 A.U.

Atom	X	Y	Z
C	-2.333979	0.366354	0.909356
N	-2.094230	1.669284	0.588258
C	-1.414759	2.158226	-0.600943
C	-0.212968	3.055701	-0.260636
C	-1.881286	-0.716912	-0.073556
N	0.915928	2.495841	0.256277
C	1.087376	1.084504	0.504092
C	0.561350	0.695710	1.894005
N	0.270166	-0.606079	2.162137
C	0.483665	-1.745462	1.285441
C	-0.778918	-2.599818	1.088173
N	-1.875491	-2.028147	0.518481
O	0.436494	1.569908	2.744160
O	-0.782924	-3.765448	1.463932
O	-2.937254	0.053533	1.926688
O	-0.303602	4.264697	-0.438435
C	-0.147408	-0.906982	3.531312
C	1.016073	-0.905401	4.505617
C	1.924315	3.408209	0.779456
C	2.902513	3.892734	-0.270865
C	-3.099365	-2.810475	0.461299
C	-3.141759	-3.713301	-0.757574
C	-2.688142	2.683182	1.458305
C	-4.184455	2.813715	1.245625
O	1.832696	-2.038115	4.272532

O	-3.222591	-2.928026	-1.939041
O	-4.414937	3.234074	-0.085976
O	3.655808	2.797417	-0.749493
C	3.223580	-1.831785	4.449443
C	3.901207	-1.457233	3.153663
C	-2.455804	-3.413965	-3.029779
C	-1.010076	-2.986284	-2.945626
C	-5.774991	3.204100	-0.451802
C	-6.323053	1.809199	-0.662409
C	4.594687	3.187903	-1.729519
C	5.245590	1.967314	-2.318147
C	4.179634	-0.128306	2.827181
C	4.735572	0.200372	1.591841
C	5.029444	-0.801192	0.669884
C	4.769762	-2.131695	0.991989
C	4.208036	-2.454214	2.222599
C	-0.645161	-1.691696	-3.328860
C	0.666433	-1.249673	-3.190076
C	1.637837	-2.100233	-2.662030
C	1.289608	-3.396541	-2.293357
C	-0.024542	-3.835784	-2.439643
C	-7.630226	1.488638	-0.297915
C	-8.142203	0.215597	-0.536026
C	-7.344086	-0.757016	-1.129972
C	-6.033275	-0.450142	-1.491151
C	-5.531864	0.827011	-1.262087
C	4.497292	1.091458	-3.109255
C	5.084146	-0.039573	-3.664906
C	6.432353	-0.311143	-3.433798
C	7.185658	0.553953	-2.647037
C	6.592200	1.686361	-2.091971
H	-2.096528	2.798532	-1.164752
H	-1.126871	1.326352	-1.244382
H	-0.904626	-0.521422	-0.508879
H	-2.574917	-0.736317	-0.919482
H	2.157206	0.857514	0.458691
H	0.636542	0.515730	-0.307647
H	1.211759	-2.418360	1.741743
H	0.892627	-1.423664	0.326287
H	-0.624381	-1.889248	3.531062
H	-0.888236	-0.165602	3.833766
H	0.627154	-0.935915	5.534372
H	1.575494	0.027666	4.385693
H	2.451797	2.897006	1.586134
H	1.412891	4.273757	1.205030
H	3.566375	4.648244	0.179876
H	2.355836	4.374639	-1.093001
H	-3.945373	-2.119890	0.467867
H	-3.153254	-3.427010	1.360636
H	-4.015131	-4.378857	-0.702626
H	-2.239753	-4.333012	-0.755524
H	-2.198327	3.634680	1.243154
H	-2.486082	2.413754	2.496328
H	-4.588823	3.555578	1.952140
H	-4.671511	1.852571	1.443288
H	3.624766	-2.780378	4.819835
H	3.409665	-1.070978	5.218809
H	-2.921175	-2.993648	-3.925860
H	-2.532595	-4.507362	-3.096385
H	-5.832976	3.771638	-1.386999

H	-6.388537	3.738124	0.290161
H	5.354965	3.851423	-1.289261
H	4.085448	3.761319	-2.520492
H	3.960574	0.657287	3.545592
H	4.928044	1.237174	1.336418
H	5.463257	-0.543237	-0.290714
H	5.008828	-2.919201	0.283568
H	3.999921	-3.492096	2.468667
H	-1.399391	-1.026934	-3.742094
H	0.934936	-0.245009	-3.503434
H	2.659972	-1.754283	-2.544546
H	2.040272	-4.068070	-1.889358
H	-0.284037	-4.851187	-2.154331
H	-8.253632	2.240015	0.180275
H	-9.161521	-0.018889	-0.245247
H	-7.738814	-1.752580	-1.306802
H	-5.399223	-1.208141	-1.941908
H	-4.511875	1.074862	-1.538503
H	3.448101	1.307065	-3.289120
H	4.494774	-0.705545	-4.287795
H	6.893306	-1.190799	-3.871634
H	8.235835	0.349855	-2.464380
H	7.183037	2.359733	-1.477279

Compound **3**

Energy: -3792.4076623 A.U.

Atom	X	Y	Z
C	0.062162	-0.995732	-3.175132
N	-1.268259	-1.023237	-2.887198
C	-2.115558	0.059154	-3.379421
C	-2.901785	0.775473	-2.270128
C	0.930083	-2.190207	-2.770072
C	1.272679	-0.119815	1.937267
N	2.169940	-1.138386	1.772645
C	2.728274	-1.243393	0.445785
C	1.693240	-1.822553	-0.526599
N	1.975378	-1.752649	-1.860118
O	1.065353	0.681720	1.040547
O	0.664714	-2.331664	-0.103129
O	0.613347	-0.054859	-3.742253
O	-4.028762	0.382413	-1.982532
C	2.316874	-2.280500	2.656948
C	3.629572	-2.240234	3.428444
C	3.195563	-1.197535	-2.423909
C	4.214063	-2.290670	-2.722292
C	-1.937355	-2.142411	-2.235509
C	-2.304748	-3.231674	-3.229995
C	-2.612001	2.758696	0.629099
N	-3.139936	1.909556	1.553046
C	-2.641637	1.980218	2.921680
C	-1.643995	0.844443	3.137541
C	-3.147237	2.701393	-0.801244
N	-0.320000	1.133229	3.307033
C	0.586338	0.012168	3.299035
N	-2.330960	1.844319	-1.658557
O	-1.725459	3.560883	0.903021
O	-2.061917	-0.306913	3.120782
C	0.265534	2.470630	3.332823

C	0.278755	3.046126	4.743084
C	-1.041504	2.360139	-2.023024
O	-1.206231	3.178753	-3.161572
C	-4.219052	1.001311	1.270328
O	-5.433112	1.721918	1.348865
H	-2.885041	-0.353188	-4.037332
H	-1.485686	0.740883	-3.948937
H	1.399161	-2.549599	-3.690986
H	0.390068	-3.011915	-2.306531
H	3.033572	-0.247507	0.118290
H	3.619251	-1.880347	0.479107
H	2.259752	-3.201038	2.067952
H	1.489199	-2.320949	3.364898
H	4.483226	-2.172410	2.733854
H	3.639143	-0.467338	-1.745139
H	2.929672	-0.655133	-3.330555
H	3.789573	-3.032835	-3.417461
H	4.467851	-2.827481	-1.791911
H	-2.848070	-1.760397	-1.772985
H	-1.307721	-2.531503	-1.431502
H	-1.393807	-3.631281	-3.709409
H	-2.937163	-2.820088	-4.035165
H	3.667158	-1.345283	4.069212
H	-3.479981	1.814972	3.601914
H	-2.243158	2.977341	3.091411
H	-3.086522	3.720962	-1.187202
H	-4.180013	2.360193	-0.856535
H	-0.010323	-0.876216	3.514485
H	1.337987	0.121862	4.089781
H	-0.250588	3.124344	2.630928
H	1.295579	2.400127	2.977984
H	-0.746586	3.227345	5.103049
H	-0.340725	1.547560	-2.232475
H	-0.657622	2.941131	-1.177397
H	-4.184108	0.196353	2.011189
H	-4.108448	0.561602	0.277570
H	0.739712	2.323676	5.438651
H	0.694790	2.870321	-3.853335
O	3.703503	-3.413380	4.191554
C	4.885042	-3.489428	4.951071
O	1.013591	4.240136	4.697054
C	1.066703	4.899062	5.939135
C	-6.548301	0.897315	1.084752
C	-7.791534	1.775691	1.125259
O	5.348261	-1.679231	-3.275989
C	6.348448	-2.619635	-3.620935
O	-2.980915	-4.239477	-2.530355
C	-3.424038	-5.282341	-3.366159
C	0.021809	3.703985	-3.621027
C	-0.290467	4.559691	-4.835848
C	-11.343040	-0.565378	0.435015
C	-10.940926	-0.267288	1.733909
C	-9.801230	0.499941	1.949937
C	-9.045382	0.982716	0.876294
C	-9.460615	0.677132	-0.420876
C	-10.599648	-0.090227	-0.642085
C	3.204662	8.616628	5.626133
C	3.134004	7.944310	6.843472
C	2.456513	6.733205	6.931651
C	1.833969	6.185311	5.809178

C	1.906144	6.862665	4.592919
C	2.591210	8.069976	4.502175
C	5.240914	-7.235763	7.042992
C	5.994735	-6.135874	7.436458
C	5.856386	-4.925053	6.764539
C	4.973575	-4.800249	5.691588
C	4.217972	-5.905772	5.300519
C	4.351737	-7.115317	5.977222
C	9.666883	-0.739139	-5.615714
C	9.875357	-1.837600	-4.791685
C	8.800787	-2.429085	-4.132530
C	7.508295	-1.937647	-4.295903
C	7.303762	-0.831994	-5.128305
C	8.377006	-0.234986	-5.778799
C	-5.662399	-8.189493	-1.116317
C	-5.015048	-8.558988	-2.292618
C	-4.275466	-7.620467	-3.006036
C	-4.183269	-6.300950	-2.558754
C	-4.835511	-5.937723	-1.381237
C	-5.566855	-6.878136	-0.662205
C	2.894510	6.857343	-6.686077
C	1.583306	7.327518	-6.656947
C	0.587926	6.580054	-6.045376
C	0.861163	5.338799	-5.453847
C	2.180609	4.879662	-5.495866
C	3.186648	5.632122	-6.105256
H	5.759841	-3.380754	4.285868
H	4.927084	-2.648861	5.661631
H	0.042549	5.100988	6.296443
H	1.545148	4.256694	6.697131
H	-6.451152	0.416758	0.099894
H	-6.621693	0.094791	1.835068
H	-7.676024	2.567061	0.375225
H	-7.836643	2.265402	2.102916
H	6.691849	-3.150386	-2.719860
H	5.916498	-3.381927	-4.291061
H	-2.570356	-5.761154	-3.873440
H	-4.068989	-4.868750	-4.160070
H	0.505040	4.317675	-2.844192
H	-0.744587	3.900132	-5.590903
H	-1.066616	5.271641	-4.540955
H	-12.233656	-1.161430	0.262036
H	-11.516780	-0.629812	2.579847
H	-9.493176	0.733043	2.965378
H	-8.884527	1.050201	-1.264650
H	-10.909184	-0.314565	-1.658119
H	3.738572	9.558755	5.552917
H	3.614832	8.358471	7.724155
H	2.414548	6.206533	7.882752
H	1.432183	6.427002	3.720544
H	2.645771	8.585341	3.548192
H	5.341384	-8.181155	7.566483
H	6.685189	-6.216537	8.269585
H	6.441378	-4.064420	7.077918
H	3.526357	-5.804365	4.473653
H	3.756696	-7.969610	5.669759
H	10.503542	-0.272357	-6.126197
H	10.876978	-2.231311	-4.653007
H	8.973376	-3.281108	-3.479866
H	6.299777	-0.440948	-5.245841

H	8.209699	0.626150	-6.417912
H	-6.233738	-8.921683	-0.554715
H	-5.077141	-9.582013	-2.650172
H	-3.762569	-7.918529	-3.916962
H	-4.752237	-4.916744	-1.027312
H	-6.063621	-6.583040	0.256680
H	3.675536	7.446254	-7.156687
H	1.341412	8.287014	-7.103715
H	-0.429434	6.960195	-6.020329
H	2.443730	3.925850	-5.061675
H	4.203234	5.251410	-6.118885

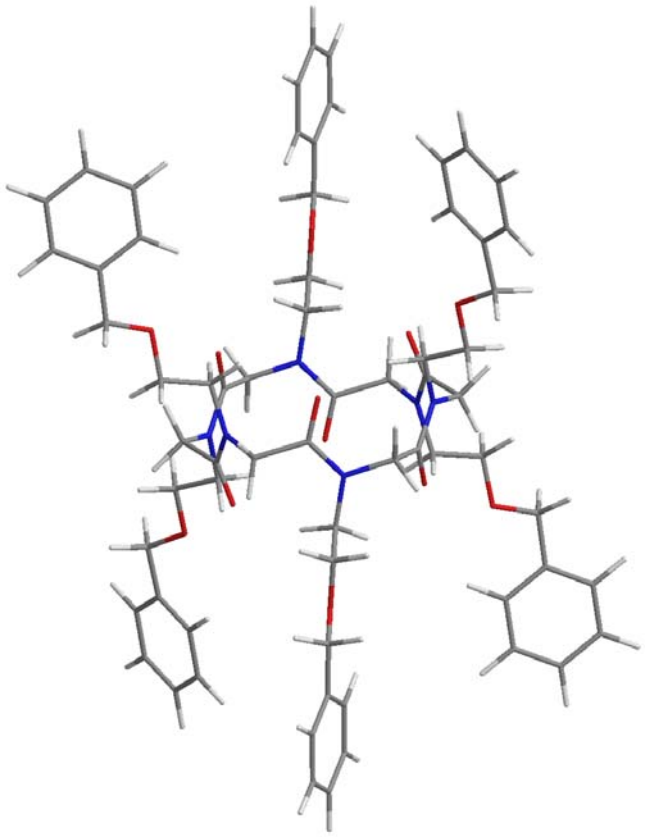


Figure S12. Structure of **3** from computational studies.

Compound **3** as a complex with $\mathbf{Na}^{+}$

Atom	X	Y	Z
C	-0.232955	2.982574	-0.280813
N	0.906504	3.604057	0.106019
C	2.138770	3.059432	-0.426895
C	2.462735	1.710394	0.236332
C	-1.561200	3.383953	0.381328
C	-2.439975	-1.684413	-0.247778
N	-3.543316	-1.004461	0.146155
C	-3.690460	0.332376	-0.391796
C	-2.679651	1.289828	0.259535
N	-2.650645	2.583742	-0.139819
O	-1.685194	-1.228433	-1.104412

O	-1.898013	0.868747	1.109677
O	-0.215589	2.090882	-1.127024
O	1.708501	1.252222	1.092269
C	-4.437935	-1.411886	1.218816
C	-5.758203	-1.962819	0.692668
C	-3.461146	3.144769	-1.209987
C	-4.602582	4.005275	-0.680983
C	0.998114	4.587081	1.174755
C	1.169806	6.006595	0.646395
C	2.703204	-1.263501	-0.269184
N	2.672927	-2.556314	0.133988
C	1.584275	-3.358452	-0.386158
C	0.254963	-2.956326	0.273623
C	3.715494	-0.305049	0.378691
N	-0.884588	-3.579573	-0.111222
C	-2.116730	-3.031946	0.418728
N	3.566549	1.031862	-0.158717
O	1.921798	-0.844008	-1.120398
O	0.236149	-2.063086	1.117973
C	-0.974750	-4.571829	-1.171385
C	-1.169884	-5.983663	-0.630617
C	4.459718	1.443126	-1.230896
C	5.783857	1.987570	-0.707349
C	3.482778	-3.115078	1.205797
C	4.623183	-3.978498	0.679274
H	2.944405	3.780402	-0.269450
H	2.023333	2.908534	-1.502817
H	-1.783074	4.440391	0.212754
H	-1.484532	3.219767	1.458707
H	-3.509015	0.303240	-1.468880
H	-4.716407	0.670845	-0.228672
H	-4.630292	-0.551494	1.865685
H	-3.961944	-2.163914	1.848182
H	-6.252407	-1.222543	0.041671
H	-3.871778	2.349788	-1.832649
H	-2.820936	3.743260	-1.864178
H	-4.212597	4.808035	-0.033331
H	-5.278957	3.394469	-0.059958
H	1.841747	4.330611	1.821583
H	0.109679	4.545470	1.804918
H	0.295821	6.290479	0.036708
H	2.052335	6.070748	-0.011661
H	-5.574937	-2.858192	0.075403
H	1.806809	-4.414399	-0.215319
H	1.508703	-3.196826	-1.463970
H	4.741045	-0.643279	0.212564
H	3.537709	-0.275657	1.456376
H	-2.002145	-2.878607	1.494425
H	-2.922897	-3.752490	0.262194
H	-0.077697	-4.550321	-1.789905
H	-1.805995	-4.310016	-1.832188
H	-0.323712	-6.255616	0.022028
H	3.985476	2.202043	-1.853089
H	4.645355	0.586603	-1.884960
H	2.841972	-3.711138	1.861644
H	3.894235	-2.318753	1.826177
H	-2.081214	-6.040739	-0.012119
H	4.232536	-4.781128	0.031861
H	5.301688	-3.369723	0.058582
H	5.601016	2.861925	-0.060930

H	6.295989	1.233293	-0.086702
O	-6.545156	-2.260557	1.807010
C	-7.815147	-2.777868	1.465572
O	-1.255769	-6.831050	-1.737249
C	-1.465093	-8.184123	-1.385029
O	5.280599	-4.503651	1.793828
C	6.374899	-5.330137	1.453329
O	-5.262490	4.530227	-1.794157
C	-6.357150	5.355399	-1.451616
O	1.308384	6.836489	1.760873
C	1.472696	8.198849	1.423254
O	6.548318	2.328826	-1.825128
C	7.826953	2.831545	-1.491991
C	8.460850	-6.696504	4.958278
C	8.544563	-7.408072	3.764437
C	7.850580	-6.969328	2.642155
C	7.074235	-5.810554	2.696596
C	6.995588	-5.100085	3.893446
C	7.682427	-5.544786	5.019605
C	-1.963321	-10.649864	-4.874042
C	-1.451804	-11.189390	-3.697264
C	-1.272777	-10.380091	-2.580262
C	-1.612709	-9.027287	-2.622803
C	-2.127226	-8.492176	-3.803434
C	-2.296664	-9.299461	-4.924289
C	-10.058105	-3.876728	4.967429
C	-10.713089	-3.557217	3.781132
C	-9.980301	-3.183483	2.659870
C	-8.586261	-3.134877	2.707909
C	-7.934756	-3.458043	3.897473
C	-8.668710	-3.822827	5.022566
C	-8.451610	6.718020	-4.952972
C	-8.536262	7.428223	-3.758369
C	-7.839698	6.990661	-2.637241
C	-7.059717	5.834405	-2.693620
C	-6.980115	5.125297	-3.891192
C	-7.669627	5.568832	-5.016189
C	1.659313	10.666876	4.941496
C	2.232574	11.096025	3.747443
C	2.185181	10.282899	2.620210
C	1.556089	9.037933	2.670077
C	0.981049	8.613955	3.867324
C	1.037264	9.423529	4.998210
C	10.177003	3.583056	-5.015268
C	10.391516	4.321460	-3.854956
C	9.612165	4.087763	-2.726678
C	8.619157	3.107508	-2.741455
C	8.409966	2.368703	-3.905683
C	9.182336	2.609779	-5.037953
H	-8.375026	-2.038995	0.872219
H	-7.687428	-3.668645	0.828171
H	-0.624936	-8.549589	-0.775301
H	-2.370754	-8.261434	-0.760665
H	7.076081	-4.764888	0.817043
H	6.026911	-6.188962	0.859229
H	-7.056267	4.789586	-0.813590
H	-6.008964	6.214967	-0.858702
H	0.623513	8.525893	0.800409
H	2.381942	8.329649	0.816904
H	7.726958	3.751112	-0.895650

H	8.353821	2.096668	-0.860845
H	8.996579	-7.040911	5.836726
H	9.144125	-8.310844	3.708796
H	7.912287	-7.535352	1.716187
H	6.385979	-4.205120	3.941314
H	7.608989	-4.987973	5.948381
H	-2.097781	-11.278208	-5.748351
H	-1.183482	-12.239806	-3.650704
H	-0.863755	-10.805762	-1.667636
H	-2.383623	-7.439557	-3.842682
H	-2.692074	-8.871703	-5.840083
H	-10.628725	-4.162108	5.845074
H	-11.796569	-3.590192	3.730792
H	-10.498656	-2.924872	1.740119
H	-6.852700	-3.411193	3.940570
H	-8.152108	-4.065836	5.945667
H	-8.989277	7.061640	-5.830535
H	-9.138467	8.329134	-3.701259
H	-7.902022	7.555769	-1.710760
H	-6.367532	4.232453	-3.940570
H	-7.595267	5.013242	-5.945640
H	1.701301	11.297241	5.823639
H	2.725397	12.061436	3.695520
H	2.643885	10.619778	1.694141
H	0.500305	7.643430	3.911726
H	0.592600	9.080767	5.9271
H	10.779475	3.768544	-5.898401
H	11.160565	5.086640	-3.830211
H	9.777997	4.674877	-1.827123
H	7.632381	1.613493	-3.923529
H	9.007021	2.033696	-5.940967
Na	0.011591	0.013167	-0.007616

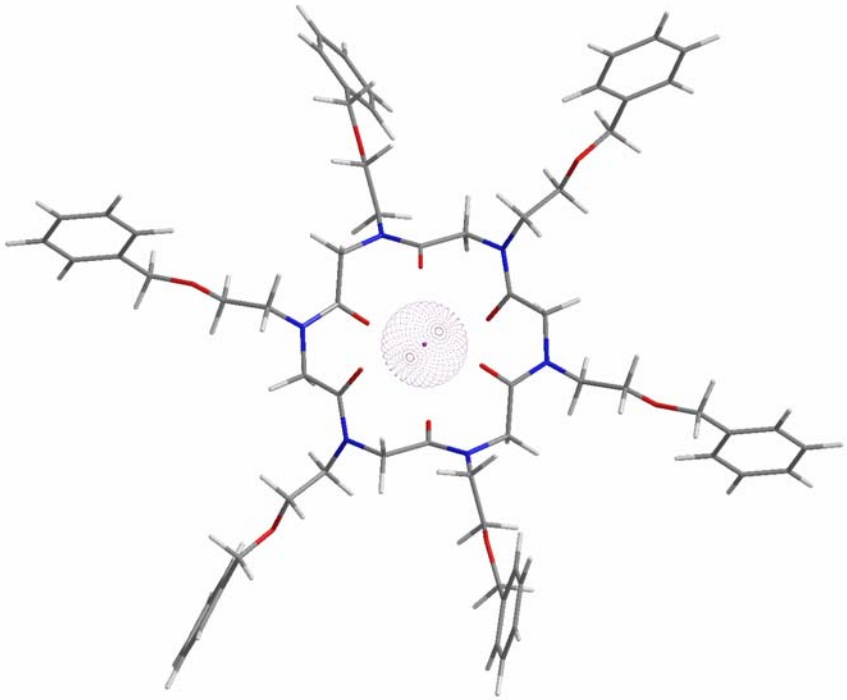


Figure S13. Structure of **3** as Na^+ complex from computational studies.

5.2 Cartesian coordinates of the considered structures, optimized at empirical level (AMBER forcefield)

Compound **1** (*cct* conformer)

Atom	X	Y	Z
C	-1.039	2.758	-1.384
C	-1.913	1.834	-2.248
N	0.094	2.198	-0.822
C	0.369	2.485	0.582
C	0.201	1.291	1.544
N	-0.831	0.373	1.373
C	-1.954	0.494	0.431
C	-1.706	-0.285	-0.879
N	-1.703	0.388	-2.101
O	0.919	1.231	2.551
O	-1.472	-1.498	-0.834
O	-1.382	3.919	-1.164
C	-0.876	-0.772	2.292
C	-1.568	-0.436	3.619
C	1.184	1.699	-1.668
C	1.840	0.394	-1.208
C	-1.746	-0.422	-3.326
C	-0.384	-0.562	-4.003
O	-0.454	-1.541	-5.040
O	2.787	0.676	-0.180
O	-2.965	-0.233	3.389
C	0.779	-1.678	-5.754
C	-3.646	0.148	4.583
C	3.329	-0.522	0.371
C	3.969	-3.261	-3.314
C	4.192	-2.141	-4.112
C	3.163	-1.632	-4.907
C	1.897	-2.236	-4.904
C	1.690	-3.371	-4.107
C	2.719	-3.877	-3.313
C	6.841	0.489	2.657
C	6.973	-0.148	1.425
C	5.837	-0.476	0.682
C	4.557	-0.175	1.168
C	4.438	0.475	2.404
C	5.574	0.803	3.146
C	-7.850	0.687	3.768
C	-7.149	1.652	4.490
C	-5.787	1.482	4.747
C	-5.109	0.347	4.278
C	-5.829	-0.619	3.561
C	-7.190	-0.448	3.304
H	-1.734	2.118	-3.291
H	-2.963	2.032	-2.004
H	-0.314	3.260	0.947
H	1.389	2.876	0.667
H	-2.846	0.047	0.884
H	-2.208	1.540	0.291
H	0.151	-1.092	2.499
H	-1.387	-1.604	1.795
H	-1.444	-1.275	4.313

H	1.933	2.500	-1.708
H	0.802	1.586	-2.685
H	2.383	-0.043	-2.053
H	1.097	-0.325	-0.854
H	-2.473	0.018	-4.019
H	-2.136	-1.422	-3.100
H	-0.078	0.398	-4.428
H	-1.134	0.463	4.069
H	0.352	-0.871	-3.257
H	0.602	-2.365	-6.589
H	1.049	-0.707	-6.186
H	-3.541	-0.633	5.344
H	-3.206	1.077	4.964
H	2.582	-1.000	1.017
H	3.586	-1.229	-0.426
H	4.771	-3.659	-2.697
H	5.170	-1.666	-4.119
H	3.357	-0.759	-5.526
H	0.715	-3.856	-4.094
H	2.543	-4.753	-2.693
H	7.725	0.747	3.234
H	7.961	-0.386	1.041
H	5.957	-0.966	-0.280
H	3.454	0.735	2.790
H	5.467	1.309	4.102
H	-8.909	0.820	3.569
H	-7.663	2.537	4.853
H	-5.258	2.245	5.314
H	-5.323	-1.509	3.193
H	-7.735	-1.203	2.743

Compound **3** as a complex with $\mathbf{NH_4^+}$

Atom	X	Y	Z
C	1.3824	2.7245	-1.0749
N	1.3684	3.2185	0.1891
C	2.3464	2.7245	1.1831
C	1.8224	1.4645	1.9101
C	0.2634	3.0845	-2.0829
C	-0.5826	-2.4145	-2.5009
N	-1.3736	-1.4755	-3.0819
C	-0.7586	-0.2935	-3.7249
C	-0.5516	0.8565	-2.7139
N	0.0374	2.0195	-3.0879
O	0.6504	-2.3165	-2.5339
O	-0.8426	0.6505	-1.5329
O	2.2324	1.8955	-1.4259
O	0.7144	1.0255	1.5901
C	-2.8426	-1.5305	-3.1099
C	-3.3646	-2.5275	-4.1539
C	0.4124	2.3325	-4.4709
C	-0.7476	2.9795	-5.2389
C	0.4194	4.2325	0.6731
C	0.7974	5.6455	0.2051
C	2.0264	-1.6395	2.4911
N	1.0644	-2.5905	2.6071
C	0.9254	-3.6575	1.5931

C	-0.0796	-3.2495	0.4941
C	2.0764	-0.4295	3.4531
N	-0.2766	-4.0285	-0.5989
C	-1.1916	-3.5685	-1.6689
N	2.6034	0.7795	2.7831
O	2.8204	-1.6515	1.5411
O	-0.6216	-2.1465	0.5861
C	0.3304	-5.3525	-0.7789
C	-0.5316	-6.4595	-0.1559
C	3.9454	1.2155	3.1281
O	3.8664	2.4335	3.7911
C	0.0804	-2.5665	3.6781
O	0.7374	-2.6495	4.9001
H	2.5374	3.5025	1.9231
H	3.3114	2.5215	0.7171
H	0.5314	4.0225	-2.5699
H	-0.6866	3.2675	-1.5849
H	0.1924	-0.5535	-4.1929
H	-1.3966	0.0565	-4.5369
H	-3.2436	-0.5435	-3.3459
H	-3.2536	-1.7485	-2.1249
H	-3.0196	-2.2465	-5.1509
H	0.7614	1.4475	-5.0039
H	1.2694	3.0085	-4.4769
H	-1.0116	3.9405	-4.7929
H	-1.6356	2.3465	-5.2139
H	0.3934	4.2255	1.7631
H	-0.6036	3.9915	0.3901
H	0.8544	5.7005	-0.8829
H	1.7734	5.9275	0.6041
H	-3.0086	-3.5375	-3.9509
H	0.5884	-4.5785	2.0681
H	1.8924	-3.8955	1.1491
H	2.6784	-0.7085	4.3181
H	1.0944	-0.1845	3.8571
H	-2.1326	-3.2825	-1.2009
H	-1.4326	-4.3875	-2.3459
H	1.3394	-5.3955	-0.3709
H	0.4594	-5.5555	-1.8429
H	-0.6856	-6.2835	0.9091
H	4.5384	1.2945	2.2151
H	4.4194	0.4705	3.7691
H	-0.5966	-3.4155	3.5701
H	-0.5156	-1.6545	3.5871
H	-1.5126	-6.4915	-0.6329
H	5.7744	3.0765	3.3181
O	-4.7766	-2.4985	-4.0979
C	-5.3926	-3.3615	-5.0459
O	0.1474	-7.6845	-0.3479
C	-0.5626	-8.8045	0.1651
C	-0.1466	-2.6115	6.0111
C	0.6754	-2.6915	7.3031
O	-0.3246	3.1575	-6.5759
C	-1.3066	3.7785	-7.3949
O	-0.2006	6.5315	0.6731
C	0.0574	7.8905	0.3461
C	5.1324	2.9385	4.1901
C	4.9294	4.2775	4.9081
C	-1.8476	-2.5805	10.8301
C	-1.5006	-3.8155	10.2521

C	-0.6796	-3.8525	9.1081
C	-0.2036	-2.6525	8.5381
C	-0.5536	-1.4155	9.1211
C	-1.3746	-1.3805	10.2651
C	1.5404	-12.5605	-0.4069
C	0.1584	-12.5555	-0.1369
C	-0.5196	-11.3335	0.0431
C	0.1794	-10.1115	-0.0489
C	1.5664	-10.1225	-0.3119
C	2.2444	-11.3445	-0.4929
C	-9.7316	-3.2935	-4.8519
C	-9.0796	-3.8435	-5.9719
C	-7.6716	-3.8595	-6.0309
C	-6.9096	-3.3225	-4.9719
C	-7.5686	-2.7765	-3.8489
C	-8.9756	-2.7605	-3.7899
C	-0.0126	4.2805	-11.5099
C	-1.3846	4.2855	-11.1929
C	-1.7996	4.1185	-9.8569
C	-0.8466	3.9405	-8.8319
C	0.5284	3.9445	-9.1539
C	0.9434	4.1115	-10.4899
C	-3.0356	10.5925	1.7581
C	-2.1616	10.9915	0.7281
C	-1.1626	10.1095	0.2711
C	-1.0346	8.8235	0.8371
C	-1.9086	8.4315	1.8741
C	-2.9086	9.3125	2.3311
C	8.6974	6.0145	6.1781
C	8.0084	5.1265	7.0271
C	6.7854	4.5635	6.6161
C	6.2444	4.8875	5.3531
C	6.9374	5.7785	4.5051
C	8.1604	6.3405	4.9181
H	-5.0846	-3.0795	-6.0539
H	-5.0686	-4.3895	-4.8799
H	-0.7336	-8.6795	1.2351
H	-1.5386	-8.8725	-0.3179
H	-0.7286	-1.6885	5.9981
H	-0.8486	-3.4455	5.9641
H	1.3874	-1.8665	7.3441
H	1.2674	-3.6075	7.3111
H	-2.2236	3.1855	-7.3849
H	-1.5516	4.7665	-7.0009
H	0.1494	7.9975	-0.7359
H	1.0034	8.2075	0.7881
H	5.6284	2.2305	4.8571
H	4.4114	4.9785	4.2531
H	4.2864	4.1405	5.7781
H	-2.4756	-2.5525	11.7091
H	-1.8616	-4.7355	10.6881
H	-0.4176	-4.8065	8.6731
H	-0.1946	-0.4895	8.6961
H	-1.6406	-0.4335	10.7121
H	2.0604	-13.4985	-0.5449
H	-0.3806	-13.4895	-0.0679
H	-1.5796	-11.3395	0.2531
H	2.1154	-9.1945	-0.3779
H	3.3054	-11.3495	-0.6969
H	-10.8116	-3.2805	-4.8069

H	-9.6596	-4.2545	-6.7859
H	-7.1796	-4.2865	-6.8929
H	-6.9976	-2.3675	-3.0279
H	-9.4766	-2.3395	-2.9299
H	0.3064	4.4105	-12.5339
H	-2.1176	4.4195	-11.9749
H	-2.8546	4.1275	-9.6229
H	1.2684	3.8195	-8.3779
H	1.9964	4.1125	-10.7329
H	-3.8016	11.2685	2.1101
H	-2.2576	11.9755	0.2911
H	-0.4936	10.4265	-0.5159
H	-1.8156	7.4525	2.3221
H	-3.5766	9.0075	3.1241
H	9.6344	6.4475	6.4961
H	8.4194	4.8795	7.9951
H	6.2644	3.8845	7.2761
H	6.5344	6.0375	3.5371
H	8.6884	7.0255	4.2691
N	1.6134	-0.6255	-0.6569
H	2.0184	0.2315	-1.0229
H	1.4374	-1.2885	-1.4069
H	0.7234	-0.3885	-0.2279
H	2.2134	-1.0335	0.0551

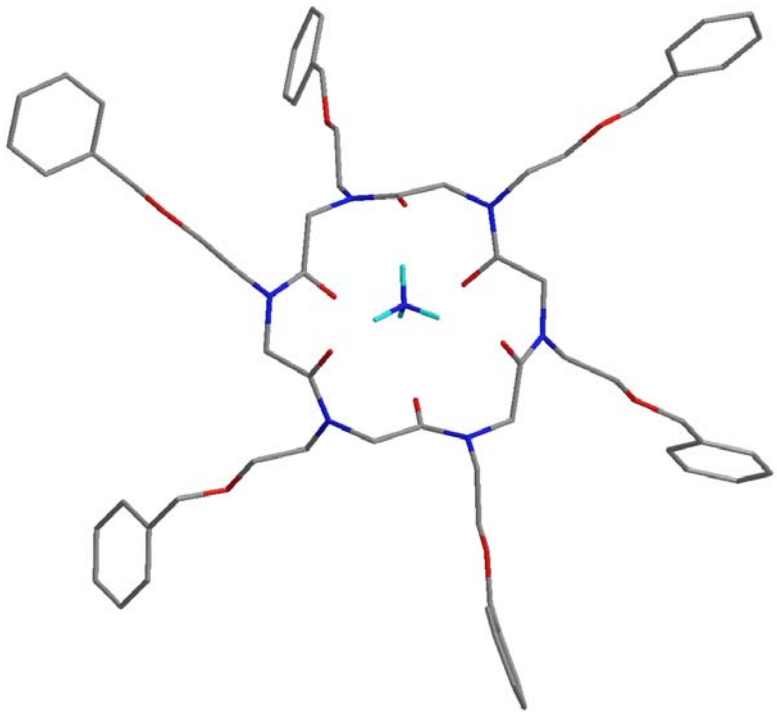


Figure S14. Structure of **3** as NH_4^+ complex from computational studies.

Compound **3** as a complex with **$BnNH_3^+$**

Atom	X	Y	Z
C	1.164	2.616	-0.384

N	0.983	2.989	0.907
C	1.984	2.589	1.911
C	1.672	1.187	2.478
C	0.131	2.988	-1.468
C	-0.550	-2.433	-2.698
N	-1.466	-1.445	-2.860
C	-1.045	-0.148	-3.426
C	-0.826	0.910	-2.323
N	0.037	1.940	-2.501
O	0.621	-2.282	-3.040
O	-1.446	0.782	-1.260
O	2.129	1.928	-0.716
O	0.484	0.877	2.641
C	-2.898	-1.586	-2.554
C	-3.634	-2.445	-3.591
C	0.877	2.126	-3.692
C	0.093	2.713	-4.875
C	-0.117	3.838	1.386
C	0.097	5.320	1.042
C	2.207	-2.081	2.235
N	1.255	-3.046	2.313
C	1.143	-4.064	1.248
C	0.061	-3.687	0.216
C	2.353	-1.011	3.335
N	0.123	-4.151	-1.057
C	-0.928	-3.761	-2.013
N	2.664	0.303	2.745
O	2.966	-2.012	1.269
O	-0.849	-2.924	0.569
C	1.155	-5.065	-1.568
C	0.858	-6.524	-1.197
C	4.065	0.607	2.494
O	4.448	1.668	3.310
C	0.358	-3.169	3.452
O	-0.574	-2.128	3.434
H	1.976	3.284	2.750
H	2.984	2.683	1.489
H	0.458	3.923	-1.924
H	-0.859	3.203	-1.070
H	-0.176	-0.263	-4.072
H	-1.832	0.216	-4.087
H	-3.375	-0.605	-2.532
H	-3.045	-1.976	-1.547
H	-3.601	-1.966	-4.571
H	1.369	1.194	-3.972
H	1.706	2.795	-3.457
H	-0.299	3.700	-4.623
H	-0.751	2.078	-5.144
H	-0.229	3.738	2.467
H	-1.068	3.490	0.994
H	0.307	5.452	-0.020
H	0.946	5.721	1.599
H	-3.184	-3.433	-3.688
H	0.879	-5.029	1.679
H	2.113	-4.228	0.783
H	3.165	-1.319	3.994
H	1.488	-0.932	3.987
H	-1.900	-3.755	-1.524
H	-1.020	-4.519	-2.792
H	2.152	-4.772	-1.242

H	1.209	-4.987	-2.655
H	0.796	-6.649	-0.115
H	4.187	0.833	1.431
H	4.677	-0.271	2.709
H	0.960	-3.175	4.364
H	-0.168	-4.125	3.398
H	-0.098	-6.830	-1.625
H	5.937	2.357	2.049
O	-4.970	-2.567	-3.146
C	-5.784	-3.326	-4.028
O	1.900	-7.331	-1.707
C	1.703	-8.716	-1.459
C	-1.413	-2.112	4.586
C	-0.772	-1.328	5.741
O	0.986	2.796	-5.965
C	0.410	3.364	-7.132
O	-1.090	6.015	1.374
C	-1.015	7.411	1.115
C	5.789	2.084	3.096
C	6.089	3.292	3.994
C	-3.403	-1.248	9.185
C	-2.480	-2.299	9.025
C	-1.624	-2.320	7.908
C	-1.684	-1.287	6.949
C	-2.608	-0.232	7.114
C	-3.466	-0.215	8.231
C	4.914	-11.217	-2.975
C	3.751	-11.801	-2.439
C	2.714	-10.984	-1.948
C	2.833	-9.579	-1.992
C	4.005	-8.998	-2.524
C	5.042	-9.815	-3.016
C	-9.881	-3.598	-2.625
C	-9.315	-4.658	-3.359
C	-7.985	-4.570	-3.815
C	-7.213	-3.424	-3.532
C	-7.789	-2.357	-2.809
C	-9.119	-2.445	-2.354
C	3.022	3.107	-10.593
C	1.879	3.929	-10.628
C	1.039	4.017	-9.499
C	1.339	3.285	-8.331
C	2.486	2.461	-8.303
C	3.326	2.374	-9.430
C	-4.775	9.396	1.984
C	-3.997	9.814	0.887
C	-2.776	9.172	0.602
C	-2.330	8.105	1.412
C	-3.104	7.703	2.520
C	-4.328	8.340	2.802
C	10.162	4.713	3.520
C	9.869	3.716	4.470
C	8.547	3.256	4.624
C	7.512	3.791	3.828
C	7.810	4.790	2.877
C	9.132	5.249	2.723
H	-5.794	-2.868	-5.019
H	-5.371	-4.331	-4.136
H	1.614	-8.892	-0.386
H	0.771	-9.043	-1.923

H	-2.351	-1.626	4.324
H	-1.682	-3.123	4.896
H	-0.542	-0.308	5.426
H	0.176	-1.777	6.038
H	-0.513	2.844	-7.388
H	0.156	4.409	-6.943
H	-0.746	7.581	0.071
H	-0.237	7.864	1.731
H	6.477	1.268	3.323
H	5.396	4.104	3.769
H	5.921	3.029	5.039
H	-4.060	-1.234	10.043
H	-2.429	-3.089	9.760
H	-0.923	-3.134	7.795
H	-2.668	0.570	6.393
H	-4.174	0.592	8.360
H	5.708	-11.843	-3.356
H	3.654	-12.877	-2.407
H	1.824	-11.441	-1.539
H	4.114	-7.924	-2.561
H	5.935	-9.366	-3.426
H	-10.902	-3.667	-2.276
H	-9.903	-5.539	-3.574
H	-7.561	-5.387	-4.381
H	-7.209	-1.470	-2.603
H	-9.557	-1.628	-1.798
H	3.665	3.037	-11.459
H	1.646	4.489	-11.522
H	0.163	4.647	-9.536
H	2.727	1.891	-7.417
H	4.202	1.742	-9.402
H	-5.712	9.890	2.202
H	-4.337	10.631	0.266
H	-2.185	9.502	-0.239
H	-2.752	6.904	3.154
H	-4.921	8.024	3.648
H	11.177	5.066	3.402
H	10.660	3.305	5.080
H	8.334	2.490	5.357
H	7.028	5.210	2.260
H	9.359	6.014	1.994
N	-1.395	-0.368	1.165
C	-2.792	-0.201	1.564
C	-3.484	3.852	2.928
C	-3.781	3.500	1.598
C	-3.553	2.184	1.149
C	-3.029	1.218	2.034
C	-2.719	1.579	3.363
C	-2.949	2.894	3.810
H	-1.258	0.132	0.288
H	-1.181	-1.357	1.026
H	-0.766	0.017	1.870
H	-3.044	-0.905	2.355
H	-3.439	-0.434	0.717
H	-3.666	4.859	3.271
H	-4.180	4.247	0.925
H	-3.785	1.929	0.124
H	-2.305	0.855	4.049
H	-2.720	3.172	4.829

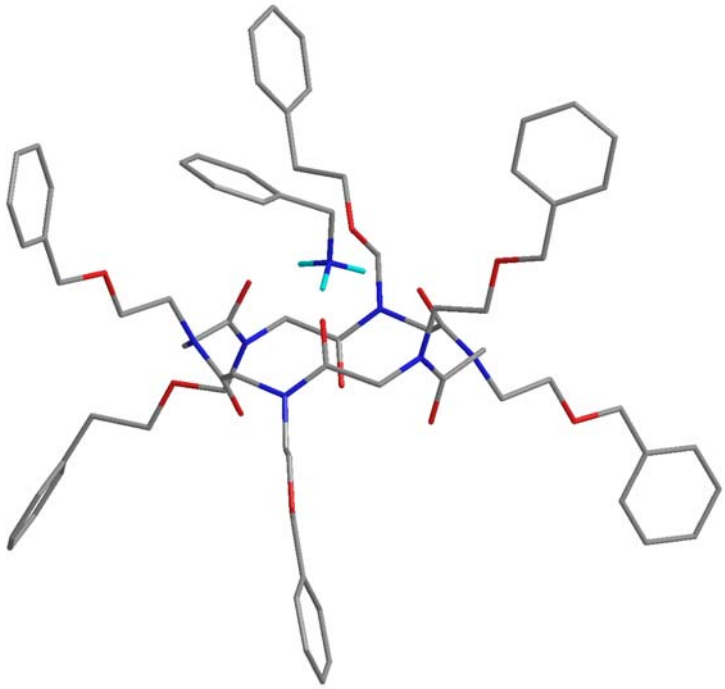


Figure S15. Structure of **3** as $BnNH_3^+$ complex from computational studies.

6.0 X-Ray studies

White needlelike crystals of **2** and yellow needles of $\mathbf{3}_2^{\cdot}[Sr(Picr)_2]_3$ were obtained according procedure reported in paragraph 1.1. Crystals suitable for X-ray diffraction analysis have been selected with size of 0.03 x 0.05 x 0.5 mm for **2** and 0.05 x 0.05 x 0.5 mm for $\mathbf{3}_2^{\cdot}[Sr(Picr)_2]_3$.

For both compounds **2** and $\mathbf{3}_2^{\cdot}[Sr(Picr)_2]_3$ diffraction data were preliminarily collected with a Rigaku AFC7S diffractometer using graphite monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å). With this conventional X-ray source crystals diffracted at 2 Å and 3 Å respectively. Higher resolution diffraction data were registered at the beamline ID23-2 of the ESRF (Grenoble, France) where the Xray beam is focussed down to 10 μm diameter (full width at half maximum). Data were collected by the oscillation technique (2° oscillation, 1 s exposure time per frame in 1 pass, 7% transmission in a 16 bunch mode, 180 frames for $\mathbf{3}_2^{\cdot}[Sr(Picr)_2]_3$) using a two-dimensional CCD detector (marMOSAIC; ~225mm diameter, 3073 x 3072 pixels and a pixel size of ~ 73 μm). The measurement was carried out at a fixed temperature of 100 (2) K using an Oxford Cryostream device. The frames were indexed and the reflections integrated in $P2_1$ (n. 4) using the XDS software suite.[5] Each reflection intensity is corrected from the action of intensity loss due to air absorption. XDS (in the CORRECT step) applies Lorentz and polarization factors as well as factors which partially compensate from damage and absorption effects to intensities and standard deviations of all reflections. These factors are determined from many symmetry-equivalent reflections usually found in the data images such that their integrated intensities become as similar as possible. Therefore, due to the small scattering volume of the crystal, absorption effect due to the crystal itself are expected to be very weak.

Data were collected up to 0.95 Å.

For **2** the overall completeness of the data is 94.6 % in the resolution shell 50-0.95 Å. For $\mathbf{3}_2^{\cdot}[Sr(Picr)_2]_3$ the overall completeness of the data is 95% in the resolution shell 50-0.95 Å. Both structures have been solved by direct methods using the program SIR97[6] and refined by means of full matrix least-squares

based on F^2 using the program SHELXL97.[7] Anisotropic thermal factors were used only for all non-hydrogen atoms.

For **2** a total of 254 refinable parameters were finally considered, final disagreement indices are R1= 0.0620 (2763 reflections $F^2>2\sigma F^2$), $_wR2$= 0.1790 (all 3129 independent. reflections).

For $\mathbf{3}_2\cdot[Sr(Picr)_2]_3$ a total of 1213 refinable parameters were finally considered, final disagreement indices are R1= 0.0680 (9365 reflections with $F^2>2\sigma F^2$), $_wR2$= 0.1788 (all 10251 independent. reflections).

The presence of an additional water molecule at hydrogen bond distance (2.62 Å) from O6 oxygen atom has been detected from the final electron density map and the corresponding oxygen atom has been included in the refinement.

‡*Crystal data for* **2***:* Formula: $C_{44}H_{52}N_4O_8$, FW=764.90, monoclinic, space group C2/c (n. 15), Z =4, a= 18.554(3) Å, b= 5.387(2), Å, c= 40.021(5) Å, β = 98.171 (5)°, V = 3959.5(17)Å^3, D_x = 1.283 gcm^{-3}, μ_{calc} =0.089 mm^{-1}.

Crystal data for $\mathbf{3}_2\cdot[Sr(Picr)_2]_3$*:* Formula: $C_{168}H_{168}N_{30}O_{66}Sr_3\cdot 2H_2O$, FW=3958.20, monoclinic, space group $P2_1/n$ (n. 14), Z =2, a= 18.895(5) Å, b= 24.546(3), Å, c= 19.252(3) Å, β = 96.304 (11)°, V = 8875(3) Å^3, D_x = 1.481 gcm^{-3}, μ_{calc} =0.355 mm^{-1}.

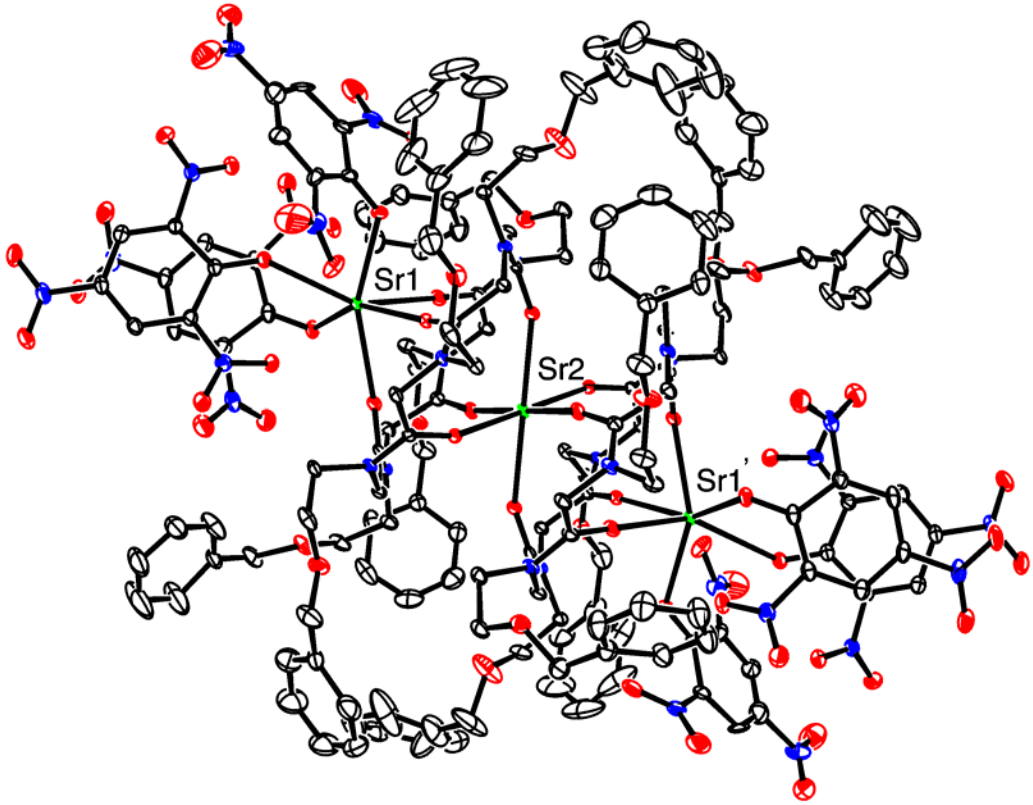


Figure S16. ORTEP drawing of $\mathbf{3}_2 \cdot [Sr(Picr)_2]_3$. Hydrogen atoms have been omitted for clarity.

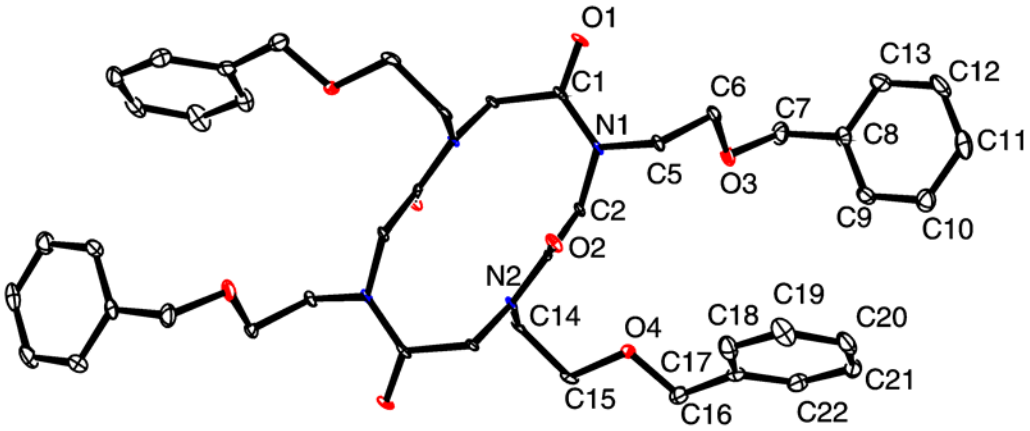


Figure S17. ORTEP drawing of **2**. Hydrogen atoms have been omitted for clarity.

7.0 Extraction studies

7.1 Determination of binding affinities for compound 3

Association constants K_{ass} were calculated from the equation $K_{ass} = K_e/K_d$, in according to methodology reported by Cram and coworkers.[8] K_d values, which represents the distribution constants of the picrate salts between water and $CHCl_3$, were previously determined by Cram,[8] while K_e were calculated following the "ultraviolet method" reported by Cram and coworkers.[9] All ultraviolet (UV) measurements were made on a Beckman DU 640 Spectrometer at 380 nm at 24-26 °C, using spectrophotometric grade solvents. The picrate salts were prepared according to literature procedures,[10] and dried under high vacuum before use. Aqueous picrate solutions were prepared that were 0.015 M for the Li^+, Na^+, K^+, NH_4^+ and 0.010 M for Rb^+ and Cs^+ salts. Aliquots of these solutions (250 μL of Li^+, Na^+, K^+, NH_4^+ and 375 μL of Rb^+ and Cs^+ solutions) were introduced in six Eppendorf vials, and to each of these, 250 μL of a solution 0.015 M of the host in $CHCl_3$ was added. The vials were capped (in order to prevent evaporation) and mixed thoroughly, using a Vortex "Maxi Mixer", for five minutes. They were finally centrifuged for 3 min, and after separation of the two phases. Aliquots of 50 μL of aqueous solution were pipetted into 5.0 mL of volumetric flasks which were brought to the mark with CH_3CN. Successively 200 μL of these solutions were diluted in 800 μL of CH_3CN. Aliquots of 100 μL of the organic phase were removed from each phase with a Hamilton syringe and diluted in 5.0 mL of CH_3CN. Successively 200 μL of this solution were diluted in 800 μL of CH_3CN. The absorbance of each sample was then measured against the appropriate blank solution at 380 nm at 25 °C. R, K_e, K_{ass} and $\Delta G°$ were thus calculated in the proper way.[8]

7.2 Extraction studies[11] for compounds 1 and 2

Equal volumes (5.0 mL) of solution at equal concentration (2.5×10^{-4} M) of compounds (in $CHCl_3$) and alkali metal picrate (Li^+, Na^+, K^+, Rb^+, Cs^+ and NH_4^+ in H_2O) were magnetically stirred for 48 h at 20 °C. The two phases were separated and the extraction percentage (A_0-$A/A_0 \times 100$) was determined by

measuring the absorbance (A) of aqueous phase at 380 nm and the corresponding absorbance (A_0) of a blank experiment. The extraction percentages were lower than 1% for all the samples of both **1** and **2**.

8.0 References

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