Supporting Information


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Material and Methods

Solvents were used without further purification. The Rink amide resin (100-200 mesh, 1% DVB, 0.68 mmol/) was used. Synthesis was carried out on Domino Blocks (www.torviq.com) in disposable polypropylene reaction vessels.

The volume of wash solvent was 10 mL per 1 g of resin. For washing, resin slurry was shaken with the fresh solvent for at least 1 min before changing the solvent. After adding a reagent solution, the resin slurry was manually vigorously shaken to break any potential resin clumps. Resin-bound intermediates were dried by a stream of nitrogen for prolonged storage and/or quantitative analysis.

For the LC/MS analysis a sample of resin (~5 mg) was treated by 50% TFA in DCM, the cleavage cocktail was evaporated by a stream of nitrogen, and cleaved compounds extracted into 1 mL of MeOH.

The LC/MS analyses were carried out using two instruments. The first one comprised a 3 x 50 mm C18 reverse phase column, 5 µm particles. Mobile phases: 10 mM ammonium acetate in HPLC grade water (A) and HPLC grade acetonitrile (B). A gradient was formed from 5% to 80% of B in 10 minutes, flow rate of 0.7 mL/min. The MS electrospray source operated at capillary voltage 3.5 kV and a desolvation temperature 300 °C. The second instrument comprised a 2.1 x 50 mm C18 reverse phase column, 2.6 µm particles, at 30°C and flow rate of 800 µL/min. Mobile phases: 10 mM ammonium acetate in HPLC grade water (A) and HPLC grade acetonitrile (B). A gradient was formed from 10% to 80% of B in 2.5 minutes; kept for 1.5 minute, flow rate of 0.8 mL/min. The column was re-equilibrated with 10% solution B for 1 minute. The APCI source operated at discharge current of 5 µA, vaporizer temperature of 400 °C and capillary temperature of 200 °C.

Purification was carried out on C18 reverse phase column 19 x 100 mm, 5 µm particles, gradient was formed from 10 mM aqueous ammonium acetate and acetonitrile, flow rate 20 mL/min.

All ¹H and ¹³C NMR experiments were performed at magnetic field strengths of 9.39 T (with operating frequencies 399.78 MHz for ¹H and 100.53 MHz for ¹³C) at ambient temperature (20 °C). ¹H spectra and ¹³C spectra were referenced relative to the signal of DMSO (¹H δ = 2.49 ppm, ¹³C δ = 39.50 ppm)

HRMS analysis was performed using LC-MS on an Orbitrap Elite high-resolution mass spectrometer (Dionex Ultimate 3000, Thermo Exactive plus, MA, USA) operating at positive full scan mode (120,000 FWHM) in the range of 100–1000 m/z. The settings for electrospray ionization were as follows: oven temperature of 150 °C and source voltage of 3.6 kV. The acquired data were internally calibrated with diisooctyl phthalate as a contaminant in CH₃OH (m/z 391.2843). Samples were diluted to a final concentration of 0.1 mg/mL in H₂O and CH₃OH (50:50, v/v). Before HPLC separation (column Phenomenex Gemini, 50 x 2.00 mm, 3 µm particles, C18), the samples were injected by direct infusion into the mass spectrometer using an autosampler. The mobile phase was isocratic CH₃CN/IPA/0.01 M ammonium acetate (40:5:55) and flow 0.3 mL/min.

Chiral analysis

HPLC chiral separation of a pair of stereoisomeric forms to determine their enantiomeric purity was carried out on Accela HPLC system (Thermo Fisher, MA, USA) equipped with PDA detector. For all analyses, cellulose tris(3,5-dimethylphenylcarbamate)-based chiral column CHIRALPAK® IB-3 (Daicel, Japan) 100 x 46 mm, particles 3 µm; maintained at 25 °C was used. The system operated at reverse phase with (A) gradient grade acetonitrile and (B) HPLC grade water. A gradient with a flow rate of 0.8 mL/min was formed from 20% solvent A, changed linearly to 50%
in 10 min, and held for 2 min. The system was returned to initial conditions in 0.5 min and then equilibrated next 2.5 min. Total analysis time was 15 min. Detection wavelength was set at 220 nm for both stereoisomers.
Experimental Section

General. The solid-phase syntheses were performed in plastic reaction vessels (syringes equipped with a porous disk) using a manually operated synthesizer. Commercially available Rink amide resin (100−200 mesh, 0.6 mmol/g) was used. The volume of wash solvent was 10 mL per 1 g of resin. For washing, the resin slurry was shaken with fresh solvent for at least 1 min before the solvent was changed. The yields of the crude products were calculated with respect to the loading of the first building block. For convenience, each procedure is described for 1 g of resin. Compounds 6a and 6b were cleaved and isolated from 500 mg and 250 mg of resin, respectively, and both peptides were cleaved from 1 g of resin.

Acylation of Rink Amide Resin with Fmoc-Ser-OH (Reins 1), Quantification, and Fmoc deprotection

Rink amide resin (1 g) was washed with DCM (3×10 mL) and DMF (3×10 mL) and treated with a solution of 50 % piperidine in DMF (10 mL) for 15 min at room temperature. The resin was thoroughly washed with DMF (5×10 mL), and DCM (3×10 mL).

The resin was treated with a solution of Fmoc-Ser-OH (2 mmol) and HOBt•H$_2$O (306 mg, 2 mmol) and DIC (312 μL, 2 mmol) in 10 mL of DCM/DCM (1:1), and the reaction slurry was shaken overnight at room temperature. The resin was washed with DMF (3×10 mL) and DCM (5×10 mL). The loading of the resin was quantified.

Quantification of Resin Loading: A sample of resin was washed 5× with DCM, 3× with MeOH and then dried with nitrogen. A 10-mg portion of resin was cleaved with 50% TFA in DCM for 30 min. The cleavage cocktail was evaporated by a stream of nitrogen, and the cleaved compound was extracted into 1 mL of MeOH. This sample of Fmoc derivate was analyzed by LC/MS, and the quantity was determined by comparison with a standard (Fmoc-Ala-OH; concentration 1 mg/mL). The loading of the resin was determined by external standard method by integration of the UV response at 300 nm.

Fmoc deprotection: The resin (1 g) was washed with DCM (3×10 mL) and DMF (3×10 mL) and treated with a solution of 50 % piperidine in DMF (10 mL) for 15 min at room temperature. The resin was thoroughly washed with DMF (5×10 mL) and DCM (3×10 mL).

Esterification with Boc-AA (Resins 2)

Resin 1 (1 g) was washed with DCM (3×10 mL) and treated with a solution of Boc-amino acid (2 mmol) and HOBt•H$_2$O (306 mg, 2 mmol), DMAP (61 mg, 0.5 mmol) and DIC (312 μL, 2 mmol) in 10 mL of DCM/DCM (1:1), and the reaction slurry was shaken overnight at room temperature. The resin was washed with DMF (3×10 mL) and DCM (5×10 mL).

Cleavage of the Boc group and acylation with bromoacetic acid (Resin 3)

Resin 4 (1 g) was washed with DCM (3×10 mL) and treated with a solution of TMSOTf (1.8 mL) and 2,6-lutidine (1.74 mL) in 10 mL of DCM for 30 min. The resin was washed with DCM (5×10 mL).

A solution of bromoacetic acid (700 mg, 5 mmol) was prepared in another syringe with a frit, and DIC (386 μL, 2.5 mmol) was added. After 5 min, DIU was removed by filtration, lutidine (292 μL, 2.5 mmol) was added, and the solution was transferred to the syringe with resin 3. The slurry was shaken for 1 h at room temperature. The resin was washed with DCM (3×10 mL).

Preparation of the triphenylphosphonium salt (Resin 4)
Resin 5 (1 g) was washed with DCM (3×10 mL) and anhydrous NMP (3×10 mL). A solution of triphenylphosphine (1.05 g, 4 mmol) in anhydrous NMP (10 mL) was added to the resin, and the slurry was shaken overnight at room temperature. The resin was washed with NMP (3×10 mL) and DCM (3×10 mL).

**Cyclization (Resin 5)**

Resins 6a (500 mg) and 6b (250 mg) were washed with DCM (3×10 mL) and anhydrous NMP (3×10 mL). A solution of TEA (70 μL, 0.5 mmol) in anhydrous NMP (5 mL) for resin 5a, or a solution of 2,6-lutidine (600 μL, 5.2 mmol) in anhydrous NMP (10 mL) for resin 5b was added to the resin, and the slurry was shaken for 2 h at room temperature for resin 5a, or at 60 °C (24 h, repeated 4x) for resin 5b. The resins were washed with NMP (3×10 mL) and DCM (3×10 mL).

**Cleavage from the resin (Compound 6)**

The cyclized resin (250 mg) was washed with DCM (3×10 mL). The resin was treated with 3 mL of a solution of 50 % TFA in DCM for 1 h at room temperature. The TFA solution was collected, and then the resin was washed with 10 % TFA in DCM (5 mL) and DCM (5 mL), and the combined extracts were concentrated under a stream of nitrogen. The crude product was dissolved in 3 mL of MeOH and purified by semi-preparative RP HPLC in MeCN/aqueous 10 mM ammonium acetate.

**Peptide synthesis**

The peptides were synthesized using an Fmoc/tBu protection strategy on Rink amide linker. The Fmoc amino acids (0.2 M solutions) were activated with DIC in the presence of HOBt in a 1:1 DCM/DMF mixture. The Fmoc group was cleaved with a solution of 50% piperidine in DMF (10 mL/g resin) for 15 min at room temperature. Final cleavage was performed with solution of 50% TFA in DCM for 1 h at room temperature. The crude products were dissolved in 10 mL of 10% AcOH in water and purified by semi-preparative RP HPLC in MeCN/aqueous 10 mM ammonium acetate.
Figure 1. Crude LC spectra of compounds 6a, 6b, 7 and 8.
Figure 2. Crude NMR spectra of compounds 6a, 6b, 7 and 8.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Temp</th>
<th>Time</th>
<th>Dilutiona</th>
<th>Scale</th>
<th>mL/g</th>
<th>SMb</th>
<th>Purityb</th>
<th>Fmoc-PG</th>
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<td>1</td>
<td>0.1 M TEA</td>
<td>RT</td>
<td>2 h</td>
<td>5 mL</td>
<td>500 mg</td>
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<td>97%</td>
<td>3%</td>
<td>stable</td>
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<td>RT</td>
<td>on</td>
<td>1 mL</td>
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<td>100</td>
<td>51%</td>
<td>26%</td>
<td>70% cleaved</td>
</tr>
<tr>
<td>3</td>
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<td>RT</td>
<td>on</td>
<td>10 mL</td>
<td>85 mg</td>
<td>130</td>
<td>34%</td>
<td>40%</td>
<td>70% cleaved</td>
</tr>
<tr>
<td>4</td>
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<td>on</td>
<td>2.5 mL</td>
<td>125 mg</td>
<td>20</td>
<td>48%</td>
<td>21%</td>
<td>cleaved</td>
</tr>
<tr>
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<td>RT</td>
<td>on</td>
<td>5 mL</td>
<td>125 mg</td>
<td>40</td>
<td>36%</td>
<td>31%</td>
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</tr>
<tr>
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<td>RT</td>
<td>on</td>
<td>10 mL</td>
<td>85 mg</td>
<td>100</td>
<td>28%</td>
<td>38%</td>
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</tr>
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<td>on</td>
<td>2.5 mL</td>
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<td>250</td>
<td>20%</td>
<td>61%</td>
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</tr>
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<td>on</td>
<td>2.5 mL</td>
<td>10 mg</td>
<td>250</td>
<td>0%</td>
<td>60%</td>
<td>cleaved</td>
</tr>
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<td>10 mg</td>
<td>250</td>
<td>30%</td>
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</tr>
<tr>
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<td>60 °C</td>
<td>2.5 mL</td>
<td>10 mg</td>
<td>250</td>
<td>0%</td>
<td>15%</td>
<td>cleaved</td>
</tr>
<tr>
<td>11</td>
<td>0.5 M prot. sp.</td>
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<td>on</td>
<td>2 mL</td>
<td>10 mg</td>
<td>200</td>
<td>23%</td>
<td>60%</td>
<td>75% cleaved</td>
</tr>
<tr>
<td>12</td>
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<td>10 mg</td>
<td>200</td>
<td>0%</td>
<td>61%</td>
<td>75% cleaved</td>
</tr>
<tr>
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<td>on</td>
<td>1 mL</td>
<td>10 mg</td>
<td>100</td>
<td>85%</td>
<td>15%</td>
<td>stable</td>
</tr>
<tr>
<td>14</td>
<td>0.5 M lutidine</td>
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<td>2.5 mL</td>
<td>125 mg</td>
<td>20</td>
<td>99%</td>
<td>1%</td>
<td>stable</td>
</tr>
<tr>
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<td>on</td>
<td>10 mL</td>
<td>85 mg</td>
<td>130</td>
<td>94%</td>
<td>6%</td>
<td>stable</td>
</tr>
<tr>
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<td>60 °C</td>
<td>on</td>
<td>10 mL</td>
<td>85 mg</td>
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<td>78%</td>
<td>21%</td>
<td>stable</td>
</tr>
<tr>
<td>17</td>
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<td>60 °C</td>
<td>5 d</td>
<td>10 mL</td>
<td>85 mg</td>
<td>130</td>
<td>1%</td>
<td>87%</td>
<td>stable</td>
</tr>
<tr>
<td>18</td>
<td>0.5 M lutidine</td>
<td>80 °C</td>
<td>on</td>
<td>2.5 mL</td>
<td>10 mg</td>
<td>250</td>
<td>0%</td>
<td>47%</td>
<td>90% cleaved</td>
</tr>
</tbody>
</table>

Note: a = standard dilution is 1 mL of reaction mixture on 100 mg of resin; b and c = estimated from LC traces.
Analytical Data of Synthetic Compounds

(9H-fluoren-9-yl)methyl (S)-(1-amino-3-((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)-1-oxopropan-2-yl)carbamate 6a

Yield 23.7 mg (49 %) of amorphous solid. \( ^1H \) NMR (400 MHz, DMSO-\( d_6 \)) \( \delta = 7.89 \) (d, \( J = 7.3 \) Hz, 2 H), 7.77 - 7.67 (m, 3 H), 7.56 (br. s., 1 H), 7.46 - 7.38 (m, 2 H), 7.36 - 7.30 (m, 2 H), 7.29 (br. s., 1 H), 5.19 (s, 1 H), 4.43 - 4.34 (m, 1 H), 4.33 - 4.28 (m, 2 H), 4.28 - 4.20 (m, 1 H), 4.18 - 4.06 (m, 2 H), 3.88 (s, 2 H), 2.79 (s, 3 H). \( ^{13}C \) NMR (101 MHz, DMSO-\( d_6 \)) \( \delta = 171.8, 171.0, 170.3, 156.0, 143.9, 143.8, 140.7, 127.7, 127.1, 125.3, 120.1, 94.9, 70.5, 65.9, 53.7, 51.7, 46.6, 28.0. HRMS (HESI-Orbitrap) \( m/z \) calcd for C\(_{23}\)H\(_{23}\)N\(_3\)O\(_5\) [M+H]\(^+\) 422.1710, found 422.1712.

(9H-fluoren-9-yl)methyl (R)-(1-amino-3-((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)-1-oxopropan-2-yl)carbamate (R)-6a

Yield 15.8 mg (40 %) of amorphous solid.

The chromatograms of chiral analysis (see General Information for experimental conditions) of (A) racemic mixture of both stereoisomeric forms, (B) (R)-6a synthesized by the use of D-serine,
and (C) (S)-6a synthesized by the use of L-serine are shown in Figure 1. Both forms, D- and L-, were stereoisomerically pure (100 % ee).

![Chromatograms](image)

Figure 1. Chromatograms of (A) racemic mixture, (B) (R)-6a synthesized from D-Ser and (C) (S)-6a synthesized from L-Ser.

(9H-fluoren-9-yl)methyl ((S)-1-amino-1-oxo-3-(((S)-5-oxo-2,3,5,7a-tetrahydro-1H-pyrrolizin-7-yl)oxy)propan-2-yl)carbamate 6b

![Chemical structure](image)

Yield 8.8 mg (42 %) of amorphous solid. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 7.89 (d, $J = 7.3$ Hz, 2 H), 7.77 - 7.68 (m, 3 H), 7.59 (br. s., 1 H), 7.42 (t, $J = 7.1$ Hz, 2 H), 7.36 - 7.28 (m, 3 H), 5.11 (s, 1 H), 4.39 (dt, $J = 4.1$, 8.2 Hz, 1 H), 4.35 - 4.26 (m, 2 H), 4.26 - 4.14 (m, 2 H), 4.14 - 4.03 (m, 2
H), 3.33 - 3.26 (m, 1 H, overlap with the water), 2.99 - 2.91 (m, 1 H), 2.07 - 1.92 (m, 3 H), 1.36 - 1.21 (m, 1 H). $^1$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 177.7, 176.8, 170.2, 156.0, 143.8, 143.7, 140.7, 127.6, 127.0, 125.3, 120.1, 94.6, 70.7, 65.8, 63.9, 53.6, 46.6, 42.8, 27.9, 27.7. HRMS (HESI-Orbitrap) $m/z$ calcd for C$_{25}$H$_{25}$N$_3$O$_5$ [M+H]$^+$ 448.1867, found 448.1869.

(2S,11S,14S)-14-carbamoyl-1-(4-hydroxyphenyl)-16-methyl-11-(((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)methyl)-3,6,9,12-tetraoxo-4,7,10,13-tetraazaheptadecan-2-aminium acetate 7

Yield 113.2 mg (53 %) of amorphous solid. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ = 8.38 (d, $J = 7.3$ Hz, 1 H), 8.24 (br. s., 1 H), 8.16 (t, $J = 5.5$ Hz, 1 H), 8.09 (d, $J = 8.2$ Hz, 1 H), 7.14 (s, 1 H), 7.03 (s, 1 H), 7.01 - 6.96 (m, 2 H), 6.70 - 6.62 (m, 2 H), 5.18 (s, 1 H), 4.70 - 4.61 (m, 1 H), 4.26 - 4.08 (m, 4 H), 3.89 (d, $J = 17.9$ Hz, 1 H), 3.83 (d, $J = 17.9$ Hz, 1 H), 3.78 (t, $J = 5.7$ Hz, 2 H), 3.73 (br. s., 2 H), 3.38 (dd, $J = 4.6$, 8.2 Hz, 1 H), 2.86 (dd, $J = 4.4$, 13.5 Hz, 1 H), 2.79 (s, 3 H), 1.88 (s, 3 H), 1.64 - 1.53 (m, 1 H), 1.53 - 1.45 (m, 2 H), 0.88 (d, $J = 6.4$ Hz, 3 H), 0.82 (d, $J = 6.4$ Hz, 3 H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ = 174.8, 174.7, 173.9, 171.8, 171.0, 169.5, 169.5, 168.1, 155.8, 130.2, 128.4, 128.4, 115.1, 95.0, 70.3, 56.3, 52.1, 51.6, 51.2, 42.1, 40.6, 28.0, 24.2, 23.1, 21.5. HRMS (HESI-Orbitrap) $m/z$ calcd for C$_{27}$H$_{39}$N$_7$O$_8$ [M+H]$^+$ 590.2933, found 590.2935.

(2S,11S,14S)-11-benzyl-14-carbamoyl-16-methyl-1-((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)-3,6,9,12-tetraoxo-4,7,10,13-tetraazaheptadecan-2-aminium acetate 8
Yield 126.0 mg (60 %) of amorphous solid. ¹H NMR (400 MHz, DMSO-d₆) δ = 8.41 (br. s., 1 H), 8.16 (t, J = 5.5 Hz, 1 H), 8.10 (d, J = 7.8 Hz, 1 H), 8.02 (d, J = 8.2 Hz, 1 H), 7.25 (d, J = 4.1 Hz, 4 H), 7.21 - 7.16 (m, 1 H), 7.14 (br. s., 1 H), 7.00 (br. s., 1 H), 5.15 (s, 1 H), 4.55 - 4.46 (m, 1 H), 4.26 - 4.17 (m, 2 H), 4.06 (br. s., 2 H), 3.88 (s, 2 H), 3.81 - 3.69 (m, 3 H), 3.66 - 3.54 (m, 2 H), 3.04 (dd, J = 4.4, 14.0 Hz, 1 H), 2.78 (s, 3 H), 2.84 - 2.75 (m, 1 H), 1.91 (br. s., 3 H), 1.62 - 1.52 (m, 1 H), 1.51 - 1.42 (m, 2 H), 0.88 (d, J = 6.4 Hz, 3 H), 0.83 (d, J = 6.4 Hz, 3 H). ¹³C NMR (101 MHz, DMSO-d₆) δ = 174.1, 172.3, 171.3, 170.8, 169.1, 168.9, 137.8, 129.3, 128.1, 126.3, 94.6, 73.5, 54.2, 53.8, 51.8, 51.1, 42.2, 42.0, 40.9, 37.4, 28.0, 24.3, 23.1, 21.6. HRMS (HESI-Orbitrap) m/z calcd for C₂₇H₃₉N₇O₇ [M+H]+ 574.2984, found 574.2980.
\(^1\)H and \(^{13}\)C NMR spectra (\(d_6\)-DMSO) of (9H-fluoren-9-yl)methyl (S)-(1-amino-3-((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)-1-oxopropan-2-yl)carbamate 6a
$^1$H and $^{13}$C NMR spectra ($d_6$-DMSO) of (9H-fluoren-9-yl)methyl ((S)-1-amino-1-oxo-3-(((S)-5-oxo-2,3,5,7a-tetrahydro-1H-pyrrolizin-7-yl)oxy)propan-2-yl)carbamate 6b
$^1$H and $^{13}$C NMR spectra ($d_6$-DMSO) of (2S,11S,14S)-14-carbamoyl-1-(4-hydroxyphenyl)-16-methyl-11-(((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)methyl)-3,6,9,12-tetraoxo-4,7,10,13-tetraazaheptadecan-2-aminium acetate 7
$^{1}$H and $^{13}$C NMR spectra ($d_6$-DMSO) of (2S,11S,14S)-11-benzyl-14-carbamoyl-16-methyl-1-((1-methyl-5-oxo-2,5-dihydro-1H-pyrrol-3-yl)oxy)-3,6,9,12-tetraoxo-4,7,10,13-tetraazaheptadecan-2-aminium acetate 8