Supplementary Materials

Swapping the Positions in a Cross Strand Lateral Ion Pairing Interaction between Ammonium- and Carboxylate-Containing Residues in a β-Hairpin

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Table S1. The $^1$H Chemical Shift Assignments for Peptide HPTDapAsp

| Residue | HN   | $\alpha$ | $\beta$ | Others          |
|---------|------|----------|--------|-----------------|
| Ac-     |      |          |        | 2.028           |
| Arg1    | 8.297| 4.399    | 1.749, 1.832 | $\gamma$: 1.607, 1.652; $\delta$: 3.201; HNt: 7.195 |
| Thr2    | 8.280| 4.724    | 4.023  | $\gamma$: 1.092 |
| Val3    | 8.684| 4.354    | 2.035  | $\gamma$: 0.897 |
| Dap4    | 8.859| 5.320    | 3.261, 3.371 |                   |
| Val5    | 8.920| 4.595    | 2.011  | $\gamma$: 0.916 |
| $^d$Pro6 |      |          |        |                  |
| Gly7    | 8.650| 3.829    | 4.005  |                  |
| Thr2    | 7.946| 4.566    | 1.779, 1.847 | $\gamma$: 1.686; $\delta$: 3.007; HNt: 7.603 |
| Asp9    | 8.536| 5.209    | 2.410, 2.545 |                   |
| Ile10   | 8.670| 4.353    | 1.848  | $\gamma$: 1.114, 1.377, 0.870 (Me); $\delta$: 0.811 |
| Leu11   | 8.421| 4.476    | 1.591  | $\gamma$: 1.591; $\delta$: 0.837, 0.884 |
| Gly7    | 8.559| 4.329    | 1.926, 2.079 | $\gamma$: 2.296, 2.322; HNt: 6.872, 7.399 |
| NH$_2$  | 7.134, 7.659 |         |        | $\gamma$: 1.597; $\delta$: 0.849, 0.902 |

$^a$Signal for the terminal HN not observed. $^b$The assignments for the minor Arg1 spin system are 8.351(HN), 4.288($\alpha$), 1.757, 1.841($\beta$), 1.598, 1.662($\gamma$), 3.200($\delta$); $^c$Thr2 spin system are 8.250(HN), 4.412($\alpha$), 4.211($\beta$); $^d$Val3 spin system are 8.210(HN), 4.173($\alpha$), 2.082($\beta$), 0.930($\gamma$); $^e$Val5 spin system are 8.115(HN), 1.880($\beta$), 0.896($\gamma$); $^f$Gln12 spin system are 8.247(HN), 4.281($\alpha$), 1.974, 2.124($\beta$), 2.363($\gamma$).

Table S2. The $^1$H Chemical Shift Assignments for Peptide HPTDabAsp

| Residue | HN   | $\alpha$ | $\beta$ | Others          |
|---------|------|----------|--------|-----------------|
| Ac-     |      |          |        | 2.030           |
| Arg1    | 8.306| 4.381    | 1.749, 1.836 | $\gamma$: 1.612, 1.657; $\delta$: 3.204; HNt: 7.195 |
| Thr2    | 8.232| 4.643    | 4.065  | $\gamma$: 1.113 |
| Val3    | 8.519| 4.252    | 2.015  | $\gamma$: 0.893 |
| Dab4    | 8.633| 4.879    | 2.986, 3.028 | $\gamma$: 2.041, 2.112 |
| Val5    | 8.595| 4.532    | 1.996  | $\gamma$: 0.921 |
| $^d$Pro6 |      |          |        |                  |
| Gly7    | 8.595| 4.413    | 1.978, 2.327 | $\gamma$: 2.038, 2.084; $\delta$: 3.812 |
| Thr2    | 8.047| 4.531    | 1.789, 1.867 | $\gamma$: 1.706; $\delta$: 3.011; HNt: 7.615 |
| Asp9    | 8.529| 4.917    | 2.493, 2.543 |                   |
| Ile10   | 8.575| 4.285    | 1.878  | $\gamma$: 1.172, 1.394, 0.884 (Me); $\delta$: 0.820 |
| Leu11   | 8.399| 4.418    | 1.597  | $\gamma$: 1.597; $\delta$: 0.849, 0.902 |
| Gln12   | 8.457| 4.308    | 1.936, 2.092 | $\gamma$: 2.316, 2.335; HNt: 6.877, 7.428 |
| NH$_2$  | 7.120, 7.618 |         |        |                  |

$^a$Signal for the terminal HN not observed. $^b$The assignments for the minor Val3 spin system are 8.188(HN), 4.120($\alpha$), 2.051($\beta$), 0.915($\gamma$); $^c$Val5 spin system are 8.107(HN), 4.125($\alpha$), 1.868($\beta$), 0.890($\gamma$); $^d$Gly7 spin system are 8.608(HN), 3.943, 4.024($\alpha$); $^e$Gln12 spin system are 8.247(HN), 4.390($\alpha$), 1.973, 2.120($\beta$), 2.365($\gamma$).
| Residue | HN  | Hα  | Hβ  | Others                |
|---------|-----|-----|-----|-----------------------|
| Ac-     | 2.042 |     |     |                       |
| Arg1<sup>b</sup> | 8.310 | 4.382 | 1.833, 1.745 | Hy: 1.655, 1.605; Hō: 3.202; HNt: 7.205 |
| Thr2    | 8.236 | 4.637 | 4.074 | Hy: 1.115             |
| Val3<sup>c</sup> | 8.505 | 4.243 | 2.009 | Hy: 0.892             |
| Orn4<sup>a</sup> | 8.455 | 4.766 | 1.728 | Hy: 1.636; Hō: 2.925, 2.873 |
| Val5<sup>d</sup> | 8.654 | 4.533 | 2.004, 1.969 | Hy: 0.924             |
| Pro6<sup>d</sup> | 8.403 |     |     |                       |
| Gly7<sup>e</sup> | 8.525 |     | 3.944, 3.889 |                       |
| Orn8    | 8.046 | 4.539 | 1.858, 1.789 | Hy: 1.699; Hō: 3.010; HNt: 7.615 |
| Asp9    | 8.510 | 4.851 | 2.549, 2.499 |                       |
| Ile10   | 8.626 | 4.275 | 1.891 | Hy: 1.401, 1.201, 0.880 (Me); Hō: 0.812 |
| Leu11   | 8.399 | 4.412 | 1.627, 1.597 | Hy: 0.902; Hō: 0.853 |
| Gln12<sup>f</sup> | 8.459 | 4.305 | 2.094, 1.941 | Hy: 2.327; HNt: 7.435 |
| NH2     | 7.620, 7.122 |     |     |                       |

<sup>a</sup>Signal for the terminal HN not observed.  
<sup>b</sup>The assignments for the minor Arg1 spin system are 8.334(HN), 4.348(Hα), 1.837(Hβ), 1.751, 1.633(Hγ);  
<sup>c</sup>Val3 spin system are 8.188(HN), 4.116(Hα), 2.048(Hβ), 0.916(Hγ);  
<sup>d</sup>Val5 spin system are 8.113(HN), 4.126(Hα), 1.879(Hβ), 0.893(Hγ);  
<sup>e</sup>Gly7 spin system are 8.606(HN), 4.308, 3.946(Hα);  
<sup>f</sup>Gln12 spin system are 8.255(HN), 4.380(Hα), 1.977, 2.129(Hβ), 2.361(Hγ).

| Residue | HN  | Hα  | Hβ  | Others                |
|---------|-----|-----|-----|-----------------------|
| Ac-     | 2.029 |     |     |                       |
| Arg1<sup>a</sup> | 8.322 | 4.375 | 1.748, 1.834 | Hy: 1.612, 1.656; Hō: 3.202; HNt: 7.216 |
| Thr2    | 8.254 | 4.606 | 4.079 | Hy: 1.125             |
| Val3<sup>b</sup> | 8.486 | 4.231 | 2.026 | Hy: 0.890             |
| Lys4    | 8.385 | 4.682 | 1.678 | Hy: 1.323; Hō: 1.575; Hα: 2.929 HNt: 7.571 |
| Val5<sup>c</sup> | 8.632 | 4.522 | 1.999 | Hy: 0.932             |
| Pro6<sup>d</sup> | 8.400 |     | 1.974, 2.340 | Hy: 2.043, 2.096; Hō: 3.773, 3.792 |
| Gly7<sup>e</sup> | 8.464 | 3.840, 3.967 |     |                       |
| Orn8<sup>f</sup> | 8.056 | 4.527 | 1.791, 1.868 | Hy: 1.702; Hō: 3.012; HNt: 7.621 |
| Asp9<sup>f</sup> | 8.503 | 4.772 | 2.541 |                       |
| Ile10   | 8.593 | 4.260 | 1.897 | Hy: 1.214, 1.409, 0.888 (Me); Hō: 0.819 |
| Leu11   | 8.396 | 4.406 | 1.633 | Hy: 1.596; Hō: 0.856, 0.906 |
| Gln12<sup>g</sup> | 8.439 | 4.302 | 1.947, 2.101 | Hy: 2.323, 2.344; HNt: 6.891, 7.462 |
| NH2     | 7.130, 7.617 |     |     |                       |

<sup>a</sup>The assignments for the minor Arg1 spin system are 8.345(HN), 4.341(Hα), 1.749, 1.835(Hβ), 1.618(Hγ);  
<sup>b</sup>Val3 spin system are 8.128(HN), 4.129(Hα), 1.882(Hβ), 0.897(Hγ);  
<sup>c</sup>Val5 spin system are 8.675(HN), 4.524(Hα), 1.997(Hβ), 0.926(Hγ);  
<sup>d</sup>Gly7 spin system are 8.614(HN), 3.946, 4.037(Hα);  
<sup>f</sup>Gln12 spin system are 7.8387(HN), 4.006(Hα), 1.848(Hβ), 1.589(Hγ);  
<sup>g</sup>Gln12 spin system are 8.313(HN), 4.293(Hα), 1.977, 2.123(Hβ), 2.346(Hγ).
Table S5. The $^1$H Chemical Shift Assignments for Peptide HPTUDapAsp

| Residue | HN  | Ha  | Hb  | Others              |
|---------|-----|-----|-----|---------------------|
| Ac-     | 2.043|     |     |                     |
| Arg1    | 8.348| 4.339| 1.757, 1.843 | Hγ: 1.6281, 1.669; Hο: 3.207; HNt: 7.207 |
| Thr2    | 8.247| 4.406| 4.204 | Hγ: 1.192          |
| Val3    | 8.224| 4.174| 2.076 | Hγ: 0.931          |
| Dap4    | 8.859| 4.815| 3.260, 3.431|                     |
| Val5    | 8.474| 4.449| 2.080 | Hγ: 0.919, 0.979   |
| Pro6    | 4.409| 1.936, 2.314| Hγ: 1.995, 2.080; Hο: 3.698, 3.887|
| Gly7    | 8.493| 3.970|     |                     |
| Orn8    | 8.224| 4.386| 1.885 | Hγ: 1.697, 1.761; Hο: 3.003; HNt:|
| Asp9    | 8.441| 4.616| 2.591, 2.698|                     |
| Ile10   | 8.082| 4.137| 1.887 | Hγ: 1.191, 1.443, 0.900 (Me); Hο: 0.861 |
| Leu11   | 8.302| 4.349| 1.683 | Hγ: 1.585, 1.619; Hο: 0.868, 0.929 |
| Gln12   | 8.266| 4.287| 1.977, 2.215| Hγ: 2.354, 2.375; HNt: 6.852, 7.543 |
| NH2     | 7.103, 7.526|     |     |                     |

*aSignal for the terminal HN not observed. bThe assignments for the minor Gly7 spin system are 8.620(HN), 3.901, 4.036(Ha), Ile10 spin system are 8.144(HN), 4.139(Ha), 1.883, 1.200, 1.442(Hb), 0.898(Hγ). |

Table S6. The $^1$H Chemical Shift Assignments for Peptide HPTUDabAsp

| Residue | HN  | Ha  | Hb  | Others              |
|---------|-----|-----|-----|---------------------|
| Ac-     | 2.040|     |     |                     |
| Arg1    | 8.337| 4.341| 1.751, 1.839 | Hγ: 1.623, 1.666; Hο: 3.204; HNt: 7.208 |
| Thr2    | 8.243| 4.379| 4.177 | Hγ: 1.185          |
| Val3    | 8.197| 4.118| 2.407 | Hγ: 0.914          |
| Dab4    | 8.637| 4.512| 3.015, 3.054| Hγ: 2.048, 2.116 |
| Val5    | 8.419| 4.420| 2.079 | Hγ: 0.934, 0.980   |
| Pro6    | 4.402| 1.939, 2.314| Hγ: 1.996, 2.078; Hο: 3.703, 3.886 |
| Gly7    | 8.468| 3.972|     |                     |
| Orn8    | 8.241| 4.379| 1.887 | Hγ: 1.700, 1.762; Hο: 3.003 |
| Asp9    | 8.437| 4.596| 2.584, 2.692|                     |
| Ile10   | 8.079| 4.132| 1.886 | Hγ: 1.185, 1.442, 0.901 (Me); Hο: 0.859 |
| Leu11   | 8.297| 4.345| 1.685 | Hγ: 1.583, 1.620; Hο: 0.867, 0.930 |
| Gln12   | 8.265| 4.284| 1.976, 2.125| Hγ: 2.352, 2.376; HNt: 6.877, 7.428 |
| NH2     | 7.103, 7.524|     |     |                     |

*aSignal for the terminal HN not observed. bThe assignments for the minor Val5 spin system are 8.132(HN), 4.241(Ha), 1.996(Hb), 0.897(Hγ); cGly7 spin system are 8.604(HN), 3.895, 4.048(Ha).
**Table S7.** The $^1$H Chemical Shift Assignments for Peptide HPTUOrnAsp

| Residue | HN   | Hα    | Hβ       | Others          |
|---------|------|-------|----------|-----------------|
| Ac-     | 2.041|       |          |                 |
| Arg1    | 8.332| 4.344 | 1.749, 1.835 | Hγ: 1.622, 1.660; Hδ: 3.205; HNt: 7.210 |
| Thr2    | 8.249| 4.374 | 4.172    | Hγ: 1.184       |
| Val3    | 8.185| 4.115 | 2.041    | Hγ: 0.913       |
| Orn4    | 8.493| 4.400 | 1.741,1.813 | Hγ: 1.657; Hδ: 3.004 |
| Val5    | 8.373| 4.420 | 2.077    | Hγ: 0.939, 0.976 |
| Orn     | 8.249| 4.373 | 1.883    | Hγ: 1.710, 1.758; Hδ: 3.003; HNt: 7.613 |
| Asp9    | 8.449| 4.598 | 2.589, 2.700 |                 |
| Ile10   | 8.077| 4.135 | 1.889    | Hγ: 1.183, 1.442, 0.904 (Me); Hδ: 0.862 |
| Leu11   | 8.298| 4.348 | 1.687    | Hγ: 0.934, 0.968 |
| Gln12   | 8.262| 4.285 | 1.979, 2.128 | Hγ: 2.353, 2.378; HNt: 6.852, 7.545 |
| NH$_2$  | 7.103, 7.524 | | | |

*aSignal for the terminal HN not observed. **The assignments for the minor Gly7 spin system are 8.597(HN), 3.893, 4.044(Hα) |

**Table S8.** The $^1$H Chemical Shift Assignments for Peptide HPTULysAsp

| Residue | HN   | Hα    | Hβ       | Others          |
|---------|------|-------|----------|-----------------|
| Ac-     | 2.306|       |          |                 |
| Arg1    | 8.327| 4.344 | 1.748, 1.832 | Hγ: 1.619, 1.660; Hδ: 3.203; HNt: 7.209 |
| Thr2    | 8.257| 4.367 | 4.165    | Hγ: 1.179       |
| Val3    | 8.184| 4.115 | 2.307    | Hγ: 0.911       |
| Lys4    | 8.423| 4.351 | 1.719, 1.766 | Hγ: 1.343, 1.418; Hδ: 1.667 |
| Val5    | 8.339| 4.419 | 2.066    | Hγ: 0.934, 0.968 |
| Pro6    | 8.457| 3.972 |         |                 |
| Gly7    | 8.457| 3.972 |         |                 |
| Orn8    | 8.243| 4.390 | 1.883    | Hγ: 1.706, 1.766; Hδ: 3.005 |
| Asp9    | 8.449| 4.596 | 2.583, 2.697 |                 |
| Ile10   | 8.072| 4.135 | 1.886    | Hγ: 1.178, 1.443, 0.904 (Me); Hδ: 0.860 |
| Leu11   | 8.301| 4.345 | 1.684    | Hγ: 1.585, 1.619 Hδ: 0.865, 0.928 |
| Gln12   | 8.263| 4.284 | 1.977, 2.126 | Hγ: 2.354, 2.375; HNt: 6.852, 7.544 |
| NH$_2$  | 7.104, 7.525 | | | |

*aSignal for the terminal HN not observed. **The assignments for the minor Val5 spin system are 7.983(HN), 4.257(Hα), 1.980(Hβ), 0.882(Hγ); *Gly7 spin system are 8.580(HN), 3.883, 4.025(Hα); Ile11 spin system are 8.129(HN), 4.137(Hα), 1.883 (Hβ), 1.139, 1.443, (Hγ); 0.897(Hδ) |
### Table S9. The $^1$H Chemical Shift Assignments for Peptide HPTFDapAsp

| Residue | HN  | $H_\alpha$ | $H_\beta$ | Others |
|---------|-----|------------|-----------|--------|
| Ac-     |     | 2.078      |           |        |
| Cys1    | 8.455 | 5.231       | 2.646, 3.169 |        |
| Arg2    | 8.764 | 4.659       | 1.826     | $H_\gamma$: 1.607, 1.652; $H_\delta$: 3.182; HNt: 7.195 |
| Thr3    | 8.647 | 4.911       | 3.903     | $H_\gamma$: 1.026 |
| Val4    | 9.202 | 4.469       | 2.006     | $H_\gamma$: 0.840 |
| Dap5$^a$| 8.886 | 5.587       | 3.226, 3.343 |        |
| Val6    | 9.194 | 4.639       | 1.989     | $H_\gamma$: 0.901 |
| $^d$Pro7| 4.347 | 1.965, 2.363 |          | $H_\gamma$: 2.073; $H_\delta$: 3.793, 3.845 |
| Gly8    | 8.800 | 3.765, 4.035 |          |        |
| Orn9    | 7.821 | 4.826       | 1.774, 1.827 | $H_\gamma$: 1.672; $H_\delta$: 3.005; HNt: 7.602 |
| Asp10   | 8.519 | 5.552       | 2.240, 2.513 |        |
| Ile11   | 9.088 | 4.482       | 1.824     | $H_\gamma$: 1.074, 1.344, 0.855 (Me); $H_\delta$: 0.798 |
| Leu12   | 8.464 | 4.732       | 1.641     | $H_\gamma$: 1.496; $H_\delta$: 0.781, 0.811 |
| Gln13   | 9.233 | 4.665       | 1.884, 2.078 | $H_\gamma$: 2.296, 2.322; HNt: 6.832, 7.333 |
| Cys14   | 9.009 | 5.093       | 3.007, 3.129 |        |
| NH$_2$  | 7.242, 7.597 |          |          |        |

$^a$Signal for the terminal HN not observed.

### Table S10. The $^1$H Chemical Shift Assignments for Peptide HPTFDabAsp

| Residue | HN  | $H_\alpha$ | $H_\beta$ | Others |
|---------|-----|------------|-----------|--------|
| Ac-     |     | 2.077      |           |        |
| Cys1    | 8.684 | 5.214       | 2.053, 2.095 |        |
| Arg2    | 8.761 | 4.670       | 1.833     | $H_\gamma$: 1.533, 1.680; $H_\delta$: 3.181; HNt: 7.132 |
| Thr3    | 8.610 | 4.932       | 3.907     | $H_\gamma$: 1.033 |
| Val4    | 9.159 | 4.397       | 1.961     | $H_\gamma$: 0.821, 0.856 |
| Dab5$^a$| 8.468 | 5.235       | 3.166     | $H_\gamma$: 2.642, 2.664 |
| Val6    | 8.830 | 4.585       | 1.940     | $H_\gamma$: 0.886, 0.901 |
| $^d$Pro7| 4.375 | 1.962, 2.342 |          | $H_\gamma$: 2.038, 2.127; $H_\delta$: 3.754, 3.867 |
| Gly8    | 8.786 | 3.894, 3.969 |          |        |
| Orn9    | 7.864 | 4.688       | 1.793, 1.844 | $H_\gamma$: 1.690 ; $H_\delta$: 3.006; HNt: 7.623 |
| Asp10   | 8.546 | 5.305       | 2.263, 2.486 |        |
| Ile11   | 9.191 | 4.463       | 1.868     | $H_\gamma$: 1.143, 1.350, 0.858 (Me); $H_\delta$: 0.797 |
| Leu12   | 8.466 | 4.706       | 1.651     | $H_\gamma$: 1.492; $H_\delta$: 0.781, 0.816 |
| Gln13   | 9.225 | 4.659       | 1.882, 2.074 | $H_\gamma$: 2.219, 2.280; HNt: 6.845, 7.310 |
| Cys14   | 9.005 | 5.080       | 3.001, 3.006 |        |
| NH$_2$  | 7.253, 7.613 |          |          |        |

$^a$Signal for the terminal HN not observed.
**Table S11.** The $^1$H Chemical Shift Assignments for Peptide HPTFOrnAsp

| Residue | HN  | Hα   | Hβ   | Others                        |
|---------|-----|------|------|-------------------------------|
| Ac-     |     |      |      |                               |
| Cys1    | 8.449 | 5.216 | 3.161, 2.661 |                            |
| Arg2$^b$ | 8.759 | 4.660 | 1.819 | Hγ: 1.683, 1.531; Hδ: 3.180; HNt: 7.123 |
| Thr3    | 8.581 | 4.950 | 3.901 | Hγ: 1.034                     |
| Val4    | 9.143 | 4.410 | 1.972 | Hγ: 0.855, 0.815               |
| Orn5$^a$ | 8.464 | 5.097 | 1.738 | Hγ: 1.597; Hδ: 2.885, 2.826    |
| Val6    | 8.919 | 4.594 | 1.963, 1.923 | Hγ: 0.910, 0.890               |
| DPro7   |     | 4.366 | 2.346, 1.961 |                                |
| Gly8    | 8.689 | 3.945, 3.871 |           |  |
| Orn9    | 7.897 | 4.667 | 1.829, 1.791 | Hγ: 1.686; Hδ: 3.007; HNt: 7.164 |
| Asp10   | 8.465 | 5.129 | 2.520, 2.270 |                             |
| Ile11   | 9.260 | 4.438 | 1.891 | Hγ: 1.364, 1.180, 0.789 (Me); Hδ: 0.855 |
| Leu12   | 8.432 | 4.697 | 1.655 | Hγ: 1.491; Hδ: 0.817, 0.78     |
| Gln13$^c$ | 9.219 | 4.666 | 2.074, 1.890 | Hγ: 2.283, 2.217; HNt: 7.289   |
| Cys14   | 8.978 | 5.081 | 3.132, 3.002 |                             |
| NH$_2$  |     |      |      | 7.604, 7.240                   |

$^a$Signal for the terminal HN not observed.

**Table S12.** The $^1$H Chemical Shift Assignments for Peptide HPTFLysAsp

| Residue | HN  | Hα   | Hβ   | Others                        |
|---------|-----|------|------|-------------------------------|
| Ac-     |     |      |      |                               |
| Cys1    | 8.464 | 5.212 | 2.665, 3.165 |                            |
| Arg2$^a$ | 8.766 | 4.668 | 1.683, 1.833 | Hγ: 1.531; Hδ: 3.178; HNt: 7.129 |
| Thr3    | 8.586 | 4.972 | 3.910 | Hγ: 0.809, 0.854               |
| Val4    | 9.118 | 4.415 | 1.978 | Hγ: 0.814, 0.855               |
| Lys5    | 8.385 | 5.012 | 1.671 | Hγ: 1.508, 1.570; Hδ: 1.266, 1.329; Hε: 2.903 |
| Val6    | 8.953 | 4.591 | 1.955 | Hγ: 0.874, 0.903               |
| DPro7   |     | 4.355 | 1.959, 2.365 | Hγ: 2.045, 2.141; Hδ: 3.809, 3.868 |
| Gly8    | 8.635 |      |      |                               |
| Orn9    | 7.917 | 4.650 | 1.790, 1.839 | Hγ: 1.682; Hδ: 3.007; HNt: 7.615 |
| Asp10   | 8.450 | 5.011 | 2.277, 2.520 |                             |
| Ile11   | 9.289 | 4.444 | 1.909 | Hγ: 1.218, 1.367, 0.859 (Me); Hδ: 0.794 |
| Leu12   | 8.419 | 4.692 | 1.659 | Hγ: 1.489; Hδ: 0.783, 0.816    |
| Gln13$^b$ | 9.226 | 4.657 | 1.892, 2.072 | Hγ: 2.218, 2.283; HNt: 6.844, 7.300 |
| Cys14   | 8.991 | 5.075 | 3.000, 3.134 |                             |
| NH$_2$  |     |      |      | 7.250, 7.614                   |

$^a$The assignments for the minor Arg2 spin system are 8.841(HN), 4.681(Hα), 1.701, 1.835(Hβ), 1.525(Hγ), 3.168(Hδ); $^b$Cys14 spin system are 8.948(HN), 5.054(Hα), 2.993, 3.143(Hβ).
### Table S13. The $^1$H Chemical Shift Assignments for Peptide HPTDapGlu

| Residue | HN   | Ha  | Hβ   | Others                  |
|---------|------|-----|------|-------------------------|
| Ac-     |      |     |      |                         |
| Arg1    | 8.304| 4.390| 1.757, 1.847 | Hγ: 1.619, 1.670; Hδ: 3.211; HNt: 7.203 |
| Thr2    | 8.180| 4.484| 4.075 | Hγ: 1.085               |
| Val3    | 8.784| 4.390| 2.015 | Hγ: 0.894               |
| Dap4a   | 8.790| 5.116| 3.300, 3.393|                       |
| Val5    | 8.858| 4.599| 1.966 | Hγ: 0.879, 0.899        |
| DPro6   |      | 4.371| 1.979, 2.354| Hγ: 2.062; Hδ: 3.794, 3.818 |
| Gly7b   | 8.710|      | 3.842, 4.021|                       |
| Orn8    | 7.988| 4.603| 1.801, 1.833 | Hγ: 1.698; Hδ: 3.008; HNt: 7.609 |
| Glu9    | 8.490| 4.420| 1.828, 1.885 | Hγ: 2.189, 2.239       |
| Ile10   | 8.819| 4.390| 1.851 | Hγ: 1.144, 1.371, 0.867 (Me); Hδ: 0.787 |
| Leu11   | 8.487| 4.419| 1.599 | Hγ: 1.599; Hδ: 0.846, 0.889 |
| Gln12   | 8.541| 4.307| 1.908, 2.062 | Hγ: 2.288, 2.311; HNt: 6.874, 7.364 |
| NH$_2$  | 7.128| 7.666|      |                         |

*aSignal for the terminal HN not observed. bThe assignments for the minor Gly7 spin system are 8.629(HN), 3.947, 4.044(Hα)*

### Table S14. The $^1$H Chemical Shift Assignments for Peptide HPTDabGlu

| Residue | HN   | Ha  | Hβ   | Others                  |
|---------|------|-----|------|-------------------------|
| Ac-     |      |     |      |                         |
| Arg1    | 8.311| 4.383| 1.754, 1.842 | Hγ: 1.618, 1.662; Hδ: 3.206; HNt: 7.206 |
| Thr2    | 8.230| 4.649| 4.106 | Hγ: 1.133               |
| Val3b   | 8.517| 4.263| 2.023 | Hγ: 0.894               |
| Dab4a   | 8.644| 4.814| 2.058, 2.105| Hγ: 2.972, 2.995        |
| Val5c   | 8.497| 4.527| 1.989 | Hγ: 0.918               |
| DPro6   |      | 4.416| 1.984, 2.329| Hγ: 2.038, 2.086; Hδ: 3.810 |
| Gly7d   | 8.549| 3.921, 3.979|      |                         |
| Orn8    | 8.092| 4.525| 1.876, 1.805 | Hγ: 1.715; Hδ: 3.016; HNt: 7.624 |
| Glu9    | 8.599| 4.557| 1.916 | Hγ: 2.169, 2.277        |
| Ile10   | 8.596| 4.293| 1.853 | Hγ: 1.160, 1.410, 0.869 (Me); Hδ: 0.812 |
| Leu11   | 8.408| 4.436| 1.602 | Hγ: 1.602; Hδ: 0.850, 0.899 |
| Gln12c  | 8.492| 4.311| 1.936, 2.086 | Hγ: 2.316, 2.336; HNt: 6.870, 7.431 |
| NH$_2$  | 7.118| 7.636|      |                         |

*aSignal for the terminal HN not observed. bThe assignments for the minor Val3 spin system are 8.267(HN), 4.127(Hα), 1.849(Hβ), 0.882(Hγ); cVal5 spin system are 8.366(HN), 4.116(Hα), 2.008(Hβ), 0.881, 0.898(Hγ); dGly7 spin system are 8.614(HN), 3.957, 4.040(Hα); eGln12 spin system are 8.340(HN), 4.298(Hα), 1.974, 2.115(Hβ), 2.367(Hγ)*
### Table S15. The $^1$H Chemical Shift Assignments for Peptide HPTOrnGlu

| Residue | HN | Ha | Hβ | Others |
|---------|----|----|----|--------|
| Ac-     | 2.032 |
| Arg1    | 8.305 | 4.386 | 1.752, 1.840, Hγ: 1.616, 1.661; Hδ: 3.206; HNt: 7.205 |
| Thr2    | 8.231 | 4.663 | 4.099 | Hγ: 1.128 |
| Val3$^b$ | 8.530 | 4.262 | 2.013 | Hγ: 0.889 |
| Orn4$^a$ | 8.477 | 4.704 | 1.758 | Hγ: 1.588, 1.656; Hδ: 2.943 |
| Val5$^c$ | 8.590 | 4.526 | 1.984 | Hγ: 0.917 |
| DPro6   | 4.409 | 1.980, 2.329 | Hγ: 2.038, 2.096; Hδ: 3.810 |
| Gly7$^d$ | 8.545 | 3.933 |
| Orn8    | 8.071 | 4.542 | 1.806, 1.874 | Hγ: 1.711; Hδ: 3.016; HNt: 7.619 |
| Glu9    | 8.565 | 4.558 | 1.910 | Hγ: 2.159, 2.257 |
| Ile10   | 8.651 | 4.305 | 1.860 | Hγ: 1.163, 1.400, 0.869 (Me); Hδ: 0.810 |
| Leu11   | 8.403 | 4.443 | 1.599 | Hγ: 1.599; Hδ: 0.849, 0.898 |
| Gln12$^e$ | 8.504 | 4.315 | 1.934, 2.085 | Hγ: 2.310, 2.335; HNt: 6.873, 7.426 |
| NH$_2$  | 7.118, 7.643 |

$^a$Signal for the terminal HN not observed. $^b$The assignments for the minor Val3 spin system are 8.268(HN), 4.122(Ha), 1.845(Hβ), 0.882(Hγ); $^c$Val5 spin system are 8.321(HN), 4.099(Ha), 2.013(Hβ), 0.808, 0.903(Hγ); $^d$Gly7 spin system are 8.610(HN), 3.955, 4.033(Hα); $^e$Gln12 spin system are 8.338(HN), 4.346(Hα), 1.977, 2.114(Hβ), 2.364(Hγ)

### Table S16. The $^1$H Chemical Shift Assignments for Peptide HPTLysGlu

| Residue | HN | Ha | Hβ | Others |
|---------|----|----|----|--------|
| Ac-     | 2.032 |
| Arg1    | 8.303 | 4.382 | 1.748, 1.836 | Hγ: 1.612, 1.656; Hδ: 3.204; HNt: 7.206 |
| Thr2    | 8.237 | 4.633 | 4.094 | Hγ: 1.128 |
| Val3$^a$ | 8.511 | 4.248 | 2.017 | Hγ: 0.888 |
| Lys4    | 8.404 | 4.687 | 1.674 | Hγ: 1.20, 1.345; Hδ: 1.599; Hε: 2.921; HNt: 7.553 |
| Val5$^b$ | 8.570 | 4.520 | 1.990 | Hγ: 0.923 |
| DPro6   | 4.398 | 1.972, 2.335 | Hγ: 2.042, 2.101; Hδ: 3.822 |
| Gly7$^c$ | 8.496 | 3.867, 3.967 |
| Orn8    | 8.041 | 4.543 | 1.797, 1.878 | Hγ: 1.715; Hδ: 3.017; HNt: 7.616 |
| Glu9    | 8.616 | 4.511 | 1.903 | Hγ: 2.138, 2.241 |
| Ile10   | 8.648 | 4.296 | 1.861 | Hγ: 1.173, 1.409, 0.873 (Me); Hδ: 0.808 |
| Leu11   | 8.392 | 4.438 | 1.598 | Hγ: 1.598; Hδ: 0.849, 0.897 |
| Gln12$^d$ | 8.496 | 4.310 | 1.934, 2.086 | Hγ: 2.315, 2.335; HNt: 6.872, 7.438 |
| NH$_2$  | 7.114, 7.631 |

$^a$The assignments for the minor Val3 spin system are 8.177(HN), 4.107(Hα), 2.041(Hβ), 0.907(Hγ); $^b$Val5 spin system are 8.268(HN), 4.122(Hα), 1.848(Hβ), 0.880(Hγ); $^c$Gly7 spin system are 8.606(HN), 3.955, 4.038(Hα); $^d$Gln12 spin system are 8.344(HN), 4.293(Hα), 1.973, 2.113(Hβ), 2.365(Hγ)
### Table S17. The $^1$H Chemical Shift Assignments for Peptide HPTUDapGlu

| Residue | HN | Hα     | Hβ     | Others                      |
|---------|----|--------|--------|-----------------------------|
| Ac-     |    | 2.044  |        |                             |
| Arg1    | 8.347 | 4.337 | 1.753, 1.842 | Hγ: 1.625, 1.665; Hδ: 3.205; HNt: 7.208 |
| Thr2    | 8.246 | 4.409 | 4.204  | Hγ: 1.191                   |
| Val3    | 8.225 | 4.173 | 2.076  | Hγ: 0.931                   |
| Dap4<sup>a</sup> | 8.856 | 4.807 | 3.257, 3.430 |
| Val5    | 8.422 | 4.453 | 2.098  | Hγ: 0.914, 0.977            |
|<sup>b</sup>Pro6 | 4.416 | 1.939, 2.320 | Hγ: 1.998, 2.076; Hδ: 3.693, 3.881 |
| Gly7<sup>b</sup> | 8.253 | 3.962, 4.000 |
| Orn8<sup>a</sup> | 8.246 | 4.379 | 1.892  | 1.706, 1.756; Hδ: 3.009      |
| Glu9<sup>c</sup> | 8.594 | 4.291 | 1.931, 2.020 | Hγ: 2.246, 2.295       |
| Ile10   | 8.234 | 4.136 | 1.856  | Hγ: 1.188, 1.477, 0.891 (Me); Hδ: 0.859 |
| Leu11   | 8.321 | 4.379 | 1.654  | Hγ: 1.596; Hδ: 0.861, 0.924  |
| Gln12   | 8.347 | 4.292 | 1.971, 2.112 | Hγ: 2.352, 2.376; HNt: 6.855, 7.532 |
| NH2     | 7.100, 7.566 |

<sup>a</sup>Signal for the terminal HN not observed. <sup>b</sup>The assignments for the minor Val5 spin system are 8.141(HN), 4.250(Hα), 1.996(Hβ), 0.900(Hγ); <sup>c</sup>Gly7 spin system are 8.637(HN), 3.908, 4.409(Hα).

### Table S18. The $^1$H Chemical Shift Assignments for Peptide HPTUDabGlu

| Residue | HN | Hα     | Hβ     | Others                      |
|---------|----|--------|--------|-----------------------------|
| Ac-     |    | 2.043  |        |                             |
| Arg1    | 8.336 | 4.341 | 1.750, 1.838 | Hγ: 1.623, 1.665; Hδ: 3.206; HNt: 7.195 |
| Thr2    | 8.243 | 4.378 | 4.179  | Hγ: 1.186                   |
| Val3    | 8.194 | 4.120 | 2.047  | Hγ: 0.923                   |
| Dab4<sup>a</sup> | 8.634 | 4.511 | 2.047, 2.114 | Hγ: 3.013, 3.054       |
| Val5<sup>b</sup> | 8.384 | 4.425 | 2.081  | Hγ: 0.934, 0982            |
|<sup>b</sup>Pro6 | 4.410 | 1.942, 2.321 | Hγ: 1.998, 2.078; Hδ: 3.703, 3.882 |
| Gly7<sup>c</sup> | 8.501 | 3.959, 4.011 |
| Orn8<sup>a</sup> | 8.260 | 4.378 | 1.765, 1.896 | Hγ: 1.709; Hδ: 3.013      |
| Glu9    | 8.605 | 4.283 | 1.933, 2.020 | Hγ: 2.238, 2.287       |
| Ile10   | 8.228 | 4.135 | 1.858  | Hγ: 1.190, 1.481, 0.889 (Me); Hδ: 0.855 |
| Leu11   | 8.320 | 4.377 | 1.654  | Hγ: 1.593; Hδ: 0.864, 0.925  |
| Gln12   | 8.347 | 4.294 | 1.977, 2.115 | Hγ: 2.356, 2.379; HNt: 6.857, 7.534 |
| NH2     | 7.101, 7.567 |

<sup>a</sup>Signal for the terminal HN not observed. <sup>b</sup>The assignments for the minor Val5 spin system are 8.141(HN), 4.250(Hα), 1.996(Hβ), 0.900(Hγ); <sup>c</sup>Gly7 spin system are 8.637(HN), 3.908, 4.409(Hα).
Table S19. The $^1$H Chemical Shift Assignments for Peptide HPTUOrnGlu

| Residue | HN  | Hα   | Hβ   | Others                        |
|---------|-----|------|------|-------------------------------|
| Ac-     | 2.043 |      |      |                               |
| Arg1    | 8.330 | 4.344 | 1.838, 1.750 | $\delta$: 3.205; $\delta$N: 7.206 |
| Thr2    | 8.249 | 4.377 | 4.175 | $\delta$: 1.183              |
| Val3$^b$ | 8.184 | 4.116 | 2.044 | $\delta$: 0.919              |
| Orn4$^a$ | 8.488 | 4.398 | 1.740, 1.816 | $\delta$: 1.656; $\delta$N: 3.008 |
| Val5    | 8.330 | 4.424 | 2.076 | $\delta$: 0.938, 0.978       |
| Pro6    |       | 4.409 | 1.943, 2.317 | $\delta$: 1.998, 2.072; $\delta$N: 3.706, 3.879 |
| Gly7$^c$ | 8.476 | 4.353 | 1.894 | $\delta$: 1.702, 1.768; $\delta$N: 3.015; $\delta$Nt: 7.624 |
| Orn8    | 8.262 | 4.373 |      |                               |
| Val3    | 8.181 | 4.115 | 2.040 | $\delta$: 0.914              |
| Lys4$^a$ | 8.418 | 4.350 | 1.714 | 7.536                         |
| Val5    | 8.290 | 4.419 | 2.068 | $\delta$: 0.934, 0.970       |
| Pro6    |       | 4.396 | 1.945, 2.311 | $\delta$: 1.988, 2.072; $\delta$N: 3.707, 3.872 |
| Gly7$^b$ | 8.486 | 3.960 | 1.895 | $\delta$: 1.711, 1.769; $\delta$N: 3.015; $\delta$Nt: 7.618 |
| Orn8    | 8.261 | 4.370 |      |                               |
| Glu9    | 8.604 | 4.287 | 2.256, 2.277 | $\delta$: 1.935, 2.022       |
| Ile10   | 8.228 | 4.135 | 1.857 | $\delta$: 1.477, 1.181, 0.891 (Me); $\delta$: 0.861 |
| Leu11   | 8.320 | 4.379 | 1.573 | $\delta$: 1.592; $\delta$N: 0.863, 0.927 |
| Gln12   | 8.344 | 4.294 | 1.970, 2.116 | $\delta$: 2.355, 2.379; $\delta$Nt: 6.857, 7.533 |
| NH$_2$  | 7.103 | 7.569 |      |                               |

$^a$Signal for the terminal HN not observed. $^b$The assignments for the minor Val3 spin system are 8.069(HN), 4.258(H$\alpha$), 1.994(H$\beta$), 0.903(H$\gamma$); $^c$Gly spin system are 8.621(HN), 3.907, 4.046(H$\alpha$)

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Table S20. The $^1$H Chemical Shift Assignments for Peptide HPTULysGlu

| Residue | HN  | Hα   | Hβ   | Others                        |
|---------|-----|------|------|-------------------------------|
| Ac-     |      |      |      |                               |
| Arg1    | 8.324 | 4.343 | 1.749, 1.833 | $\delta$: 1.620, 1.659; $\delta$N: 3.202; $\delta$Nt: 7.206 |
| Thr2    | 8.258 | 4.370 | 4.166 | $\delta$: 1.180              |
| Val3$^a$ | 8.181 | 4.115 | 2.040 | $\delta$: 0.914              |
| Val5    | 8.290 | 4.419 | 2.068 | $\delta$: 0.934, 0.970       |
| Lys4$^a$ | 8.418 | 4.350 | 1.714 | 7.536                         |
| Pro6    |       | 4.396 | 1.945, 2.311 | $\delta$: 1.988, 2.072; $\delta$N: 3.707, 3.872 |
| Gly7$^b$ | 8.486 | 3.960 | 1.895 | $\delta$: 1.711, 1.769; $\delta$N: 3.015; $\delta$Nt: 7.618 |
| Orn8    | 8.261 | 4.370 |      |                               |
| Glu9    | 8.604 | 4.287 | 2.256, 2.277 | $\delta$: 1.935, 2.022       |
| Ile10   | 8.228 | 4.135 | 1.857 | $\delta$: 1.477, 1.181, 0.891 (Me); $\delta$: 0.861 |
| Leu11   | 8.320 | 4.379 | 1.573 | $\delta$: 1.592; $\delta$N: 0.863, 0.927 |
| Gln12   | 8.344 | 4.294 | 1.970, 2.116 | $\delta$: 2.355, 2.379; $\delta$Nt: 6.857, 7.533 |
| NH$_2$  | 7.102 | 7.568 |      |                               |

$^a$The assignments for the minor Val3 spin system are 7.985(HN), 4.261(H$\alpha$), 1.990(H$\beta$), 0.903(H$\gamma$); $^b$Gly7 spin system are 8.607(HN), 3.902, 4.039(H$\alpha$),
### Table S21. The $^1$H Chemical Shift Assignments for Peptide HPTFDapGlu.

| Residue | HN   | $H_\alpha$ | $H_\beta$ | Others |
|---------|------|------------|------------|--------|
| Ac-     | 2.083|            |            |        |
| Cys1    | 8.446| 5.219      | 2.678, 3.168|        |
| Arg2    | 8.752| 4.688      | 1.830, 1.860| $H_Y$: 1.535, 1.686; $H_\delta$: 3.185; $H_{Nt}$: 7.131 |
| Thr3    | 8.558| 5.017      | 3.948      | $H_Y$: 1.077 |
| Val4    | 9.223| 4.475      | 2.000      | $H_Y$: 0.846 |
| Dap5    | 8.875| 5.287      | 3.309, 3.371|        |
| Val6    | 9.035| 4.638      | 1.941      | $H_Y$: 0.866, 0.890 |
| DPro7   | 4.344| 1.974, 2.367| $H_Y$: 2.050, 2.093; $H_\delta$: 3.771, 3.848 |
| Gly8    | 8.381| 3.804, 4.041|            |        |
| Orn9    | 7.908| 4.690      | 1.811      | $H_Y$: 1.688; $H_\delta$: 3.006; $H_{Nt}$: 7.610 |
| Glu10   | 8.423| 5.038      | 1.745, 1.879| $H_Y$: 2.142, 2.191 |
| Ile11   | 9.078| 4.470      | 1.832      | $H_Y$: 1.111, 1.337, 0.866 (Me); $H_\delta$: 0.777 |
| Leu12   | 8.508| 4.655      | 1.685      | $H_Y$: 1.496; $H_\delta$: 0.787, 0.828 |
| Gln13   | 9.225| 4.664      | 1.887, 2.067| $H_Y$: 2.220, 2.278; $H_{Nt}$: 6.825, 7.303 |
| Cys14   | 8.974| 5.083      | 3.006, 3.134|        |
| NH$_2$  | 7.242, 7.605|            |            |        |

$^a$Signal for the terminal HN not observed.

### Table S22. The $^1$H Chemical Shift Assignments for Peptide HPTFDabGlu

| Residue | HN   | $H_\alpha$ | $H_\beta$ | Others |
|---------|------|------------|------------|--------|
| Ac-     | 2.083|            |            |        |
| Cys1    | 8.450| 5.215      | 2.657, 3.168|        |
| Arg2    | 8.758| 4.683      | 1.825, 1.852| $H_Y$: 1.544, 1.685; $H_\delta$: 3.186; $H_{Nt}$: 7.195 |
| Thr3    | 8.583| 4.950      | 3.948      | $H_Y$: 1.069 |
| Val4    | 9.120| 4.445      | 1.985      | $H_Y$: 0.815, 0.854 |
| Dab5    | 8.710| 5.130      | 2.074, 2.101| $H_Y$: 2.931, 2.966 |
| Val6    | 8.599| 4.586      | 1.913      | $H_Y$: 0.870, 0.899 |
| DPro7   | 4.380| 1.969, 2.347| $H_Y$: 2.043, 2.133; $H_\delta$: 3.744, 3.867 |
| Gly8    | 8.775| 3.906, 3.994|            |        |
| Orn9    | 7.938| 4.703      | 1.823, 1.869| $H_Y$: 1.705; $H_\delta$: 3.011; $H_{Nt}$: 7.624 |
| Glu10   | 8.567| 4.910      | 1.998, 2.228| $H_Y$: 1.783, 1.878 |
| Ile11   | 9.052| 4.492      | 1.834      | $H_Y$: 1.094, 1.329, 0.851 (Me); $H_\delta$: 0.789 |
| Leu12   | 8.450| 4.715      | 1.658      | $H_Y$: 1.499 $H_\delta$: 0.785, 0.820 |
| Gln13   | 9.207| 4.660      | 1.879, 2.078| $H_Y$: 2.214, 2.272; $H_{Nt}$: 6.826, 7.320 |
| Cys14   | 8.989| 5.083      | 3.006, 3.134|        |
| NH$_2$  | 7.241, 7.605|            |            |        |

$^a$Signal for the terminal HN not observed.
Table S23. The $^1$H Chemical Shift Assignments for Peptide HPTFOrnGlu

| Residue | HN | H$\alpha$ | H$\beta$ | Others |
|---------|----|-----------|-----------|--------|
| Ac-     | 2.077 |           |           |        |
| Cys1    | 8.468 | 5.213     | 2.649, 3.167 |        |
| Arg2    | 8.770 | 4.679     | 1.824     | Hy: 1.687; H$\delta$: 3.182; HNt: 7.134 |
| Thr3    | 8.599 | 4.946     | 3.939     | Hy: 1.060 |
| Val4    | 9.137 | 4.423     | 1.971     | Hy: 0.814, 0.851 |
| Orn5    | 8.555 | 4.954     | 1.753, 1.807 | Hy: 1.580, 1.653; H$\delta$: 2.933 |
| Val6    | 8.767 | 4.571     | 1.924     | Hy: 0.870, 0.895 |
| DPro7   | 4.376 | 1.969, 2.335 |        | Hy: 2.036, 2.134; H$\delta$: 3.724, 3.864 |
| Gly8    | 8.754 | 3.934     |           |        |
| Orn9    | 7.953 | 4.688     | 1.817, 1.862 | Hy: 1.698; H$\delta$: 3.008; HNt: 7.603 |
| Glu10   | 8.515 | 4.947     | 1.778, 1.877 | Hy: 2.000, 2.208 |
| Ile11   | 9.103 | 4.496     | 1.844     | Hy: 1.109, 1.324, 0.848 (Me); H$\delta$: 0.789 |
| Leu12   | 8.447 | 4.725     | 1.653     | Hy: 1.492; H$\delta$: 0.780, 0.814 |
| Gln13   | 9.220 | 4.659     | 1.872, 2.072 | Hy: 2.212, 2.269; HNt: 6.840, 7.329 |
| Cys14   | 9.008 | 3.001, 3.133 |        |        |

NH$_2$  7.254, 7.615

$^a$Signal for the terminal HN not observed.

Table S24. The $^1$H Chemical Shift Assignments for Peptide HPTFLysGlu

| Residue | HN | H$\alpha$ | H$\beta$ | Others |
|---------|----|-----------|-----------|--------|
| Ac-     | 2.080 |           |           |        |
| Cys1    | 8.449 | 5.211     | 2.656, 3.170 |        |
| Arg2    | 8.758 | 4.682     | 1.837     | Hy: 1.541, 1.683; H$\delta$: 3.182; HNt: 7.128 |
| Thr3    | 8.575 | 4.953     | 3.941     | Hy: 1.061 |
| Val4    | 9.083 | 4.420     | 1.975     | Hy: 0.814, 0.853 |
| Lys5$^a$| 8.462 | 4.947     | 1.670, 1.708 | Hy: 1.225, 1.313; H$\delta$: 1.606; H$\epsilon$: 2.906 |
| Val6    | 8.758 | 4.575     | 1.937     | Hy: 0.878, 0.903 |
| DPro7   | 4.368 | 1.959, 2.350 | Hy: 2.041, 2.139; H$\delta$: 3.767, 3.857 |
| Gly8    | 8.672 | 3.855, 3.970 |        |        |
| Orn9    | 7.938 | 4.674     | 1.810, 1.868 | Hy: 1.691; H$\delta$: 3.011; HNt: 7.615 |
| Glu10   | 8.555 | 4.817     | 1.781, 1.871 | Hy: 1.982, 2.191 |
| Ile11   | 8.398 | 4.492     | 1.851     | Hy: 1.120, 1.341, 0.854 (Me); H$\delta$: 0.789 |
| Leu12   | 8.398 | 4.724     | 1.650     | Hy: 1.495; H$\delta$: 0.782, 0.817 |
| Gln13   | 9.203 | 4.662     | 1.875, 2.075 | Hy: 2.209, 2.272; HNt: 6.829, 7.321 |
| Cys14   | 8.986 | 5.076     | 3.004, 3.131 |        |

NH$_2$  7.238, 7.603
Table S25. The $^1$H Chemical Shift Assignments for Peptide HPTDapAad

| Residue | HN     | $\alpha$ | $\beta$ | Others              |
|---------|--------|----------|---------|---------------------|
| Ac-     | 8.328  | 4.376    | 1.757, 1.844 | $\gamma$: 1.665; $\delta$: 3.207; HNt: 7.207 |
| Thr2    | 8.246  | 4.606    | 4.119   | $\gamma$: 1.155    |
| Val3$^a$| 8.464  | 4.290    | 2.077   | $\gamma$: 0.912    |
| Dap4$^b$| 8.872  | 5.001    | 3.269, 3.418 |
| Val5$^c$| 8.543  | 4.555    | 2.025   | $\gamma$: 0.912    |
| $^d$Pro6| 4.423  | 1.597, 2.330 | $\gamma$: 1.986, 2.049; HNt: 3.790, 3.836 |
| Gly7$^d$| 8.508  | 3.922, 3.954 |
| Orn8$^e$| 8.120  | 4.488    | 1.799, 1.874 | $\gamma$: 1.710; $\delta$: 3.017; HNt: |
| Aad9    | 8.475  | 4.512    | 1.612, 1.697 | $\gamma$: 2.191; $\delta$: 1.490 |
| Ile10   | 8.451  | 4.258    | 1.835   | $\gamma$: 1.154, 1.418, 0.869(Me); $\delta$: 0.820 |
| Leu11   | 8.397  | 4.428    | 1.596   | $\gamma$: 1.831; $\delta$: 0.850 |
| Gln12$^f$| 8.470  | 4.302    | 1.944, 2.083 | $\gamma$: 2.337; HNt: 6.867 |
| NH$_2$  | 7.118  | 7.635    |

$^a$The assignments for the minor Val3 spin system are 8.128(HN), 4.178 ($\alpha$), 2.080($\beta$), 0.931($\gamma$); $^b$Signal for the terminal HN not observed; $^c$Val5 spin system are 8.279(HN), 4.127($\alpha$), 1.833($\beta$), 0.879($\gamma$); $^d$Gly7 spin system are 8.613(HN), 3.926, 4.029($\delta$); $^e$Orn8 spin system are 8.361(HN), 4.193($\alpha$), 1.753, 1.855($\beta$), 1.677($\gamma$); $^f$Gln12 spin system are 8.357(HN), 4.344($\alpha$), 1.975, 2.111($\beta$), 2.365($\gamma$).

Table S26. The $^1$H Chemical Shift Assignments for Peptide HPTDabAad

| Residue | HN     | $\alpha$ | $\beta$ | Others              |
|---------|--------|----------|---------|---------------------|
| Ac-     | 8.309  | 4.394    | 1.754, 1.842 | $\gamma$: 1.614, 1.659; $\delta$: 3.207; HNt: 7.206 |
| Arg1$^a$| 8.248  | 4.681    | 4.077   | $\gamma$: 1.133    |
| Thr2    | 8.547  | 4.287    | 2.013   | $\gamma$: 0.890    |
| Val3$^b$| 8.667  | 4.887    | 2.964   | $\gamma$: 2.021, 2.108 |
| Dab4$^c$| 8.527  | 4.544    | 2.068   | $\gamma$: 0.918    |
| Val5$^d$| 8.409  | 4.436    | 1.593   | $\gamma$: 1.706; $\delta$: 0.845, 0.894 |
| $^d$Pro6| 4.409  | 1.980, 2.330 | $\gamma$: 2.041, 2.098; $\delta$: 3.206, 3.815 |
| Gly7$^e$| 8.569  | 3.943    |
| Orn8$^f$| 8.060  | 4.558    | 1.806, 1.870 | $\gamma$: 1.711; $\delta$: 3.015; HNt: 7.622 |
| Aad9    | 8.529  | 4.597    | 1.633, 1.696 | $\gamma$: 2.174; $\delta$: 1.450 |
| Ile10   | 8.606  | 4.313    | 1.841   | $\gamma$: 1.139, 1.399, 0.865(Me); $\delta$: 0.807 |
| Leu11   | 8.409  | 4.453    | 1.593   | $\gamma$: 1.706; $\delta$: 0.845, 0.894 |
| Gln12$^g$| 8.529  | 4.306    | 1.940, 2.085 | $\gamma$: 2.321; HNt: 6.872, 7.428 |
| NH$_2$  | 7.126  | 7.656    |

$^a$The assignments for the minor Arg1 spin system are 8.337(HN), 4.358($\alpha$), 1.757, 1.843($\beta$), 1.579, 1.653($\gamma$), 3.212($\delta$).$^b$Val3 spin system are 8.275(HN), 4.128 ($\alpha$), 1.838($\beta$), 0.877($\gamma$); $^c$Signal for the terminal HN not observed; $^d$Val5 spin system are 8.194(HN), 4.124($\alpha$), 2.054($\beta$), 0.921($\gamma$); $^e$Gly7 spin system are 8.606(HN), 4.024($\alpha$); $^f$Orn8 spin system are 8.364(HN), 4.360($\alpha$), 1.880($\beta$), 1.755($\gamma$); $^g$Gln12 spin system are 8.359(HN), 4.295($\alpha$), 1.975 ($\beta$), 2.369($\gamma$).
Table S27. The $^1$H Chemical Shift Assignments for Peptide HPTOrnAad

| Residue | HN  | $\mathrm{H}^\alpha$ | $\mathrm{H}^\beta$ | Others                  |
|---------|-----|----------------------|---------------------|-------------------------|
| Ac-     |     |                      |                     |                         |
| Arg1    | 8.302 | 4.401 | 1.751, 1.840 | H$_\gamma$: 1.610, 1.659; H$_\delta$: 3.205; HN$_{t}$: 7.201 |
| Thr2    | 8.243 | 4.728 | 4.057   | H$_\gamma$: 1.118       |
| Val3$^a$ | 8.587 | 4.295 | 2.005   | H$_\gamma$: 0.880       |
| Orn4$^b$ | 8.493 | 4.766 | 1.719, 1.770 | H$_\gamma$: 1.570, 1.646; H$_\delta$: 2.933 |
| Val5$^b$ | 8.663 | 4.544 | 1.975   | H$_\gamma$: 0.913       |
| dPro6   |     |                      |                     |                         |
| Gly7    | 8.583 | 4.582 | 1.805, 1.863 | H$_\gamma$: 1.703; H$_\delta$: 3.012; HN$_{t}$: 7.618 |
| Aad9    | 8.507 | 4.639 | 1.611, 1.684 | H$_\gamma$: 2.165; H$_\delta$: 1.432 |
| Ile10   | 8.702 | 4.336 | 1.848   | H$_\gamma$: 1.145, 1.390, 0.863(Me); H$_\delta$: 0.799 |
| Leu11   | 8.409 | 4.461 | 1.589   | H$_\gamma$: 1.711; H$_\delta$: 0.845, 0.886 |
| Gln12$^c$ | 8.547 | 4.310 | 1.921, 2.075 | H$_\gamma$: 2.312; HN$_{t}$: 6.876, 7.406 |
| NH$_2$  | 7.128 | 7.665 |                     |                         |

$^a$The assignments for the minor Val3 spin system are 8.189(HN), 4.114(H$_\alpha$), 2.047(H$_\beta$), 0.914(H$_\gamma$); $^b$Signal for the terminal HN not observed; $^c$The assignments for the minor Gln12 spin system are 8.358(HN), 4.295(H$_\alpha$), 1.974(H$_\beta$), 2.364(H$_\gamma$).

Table S28. The $^1$H Chemical Shift Assignments for Peptide HPTLysAad

| Residue | HN  | $\mathrm{H}^\alpha$ | $\mathrm{H}^\beta$ | Others                  |
|---------|-----|----------------------|---------------------|-------------------------|
| Ac-     |     |                      |                     |                         |
| Arg1    | 8.350 | 4.388 | 1.748, 1.831 | H$_\gamma$: 1.608, 1.655; H$_\delta$: 3.202; HN$_{t}$: 7.226 |
|Thr2    | 8.306 | 4.698 | 4.063   | H$_\gamma$: 1.122       |
| Val3$^a$ | 8.599 | 4.273 | 2.008   | H$_\gamma$: 0.879       |
| Lys4$^b$ | 8.461 | 4.770 | 1.653   | H$_\gamma$: 1.200, 1.303; H$_\epsilon$: 2.894 |
| Val5$^c$ | 8.678 | 4.540 | 1.978   | H$_\gamma$: 0.922       |
| dPro6   |     |                      |                     |                         |
| Gly7$^d$ | 8.580 | 4.386 | 1.970, 2.346 | H$_\gamma$: 2.042, 2.111; H$_\delta$: 3.834 |
| Orn8    | 8.020 | 4.591 | 1.795, 1.867 | H$_\gamma$: 1.694; H$_\delta$: 3.010; HN$_{t}$: 7.158 |
| Aad9    | 8.610 | 4.556 | 1.617, 1.690 | H$_\gamma$: 2.152, 2.186; H$_\delta$: 1.444 |
| Ile10$^e$ | 8.747 | 4.317 | 1.857   | H$_\gamma$: 1.168, 1.394, 0.864(Me); H$_\delta$: 0.796 |
| Leu11   | 8.452 | 4.451 | 1.589   | H$_\gamma$: 0.842, 0.891 |
| Gln12$^f$ | 8.581 | 4.303 | 1.932, 2.080 | H$_\gamma$: 2.318; HN$_{t}$: 6.920 |
| NH$_2$  | 7.703 |                      |                     |                         |

$^a$The assignments for the minor Val3 spin system are 8.208(HN), 4.038(H$_\alpha$), 2.034(H$_\beta$), 0.955(H$_\gamma$); $^b$Signal for the terminal HN not observed; $^c$The assignments for the minor Val5 spin system are 8.243(HN), 4.104(H$_\alpha$), 2.034(H$_\beta$), 0.913(H$_\gamma$); $^d$The assignments for the minor Gly7 spin system are 8.644(HN), 3.929, 4.017(H$_\alpha$); $^e$The assignments for the minor Ile10 spin system are 8.374(HN), 4.075(H$_\alpha$), 1.744(H$_\beta$), 0.798, 0.902(H$_\gamma$); $^f$The assignments for the minor Gln12 spin system are 8.422(HN), 4.302(H$_\alpha$), 1.971, 2.113(H$_\beta$), 2.369(H$_\gamma$).
Table S29. The $^1$H Chemical Shift Assignments for Peptide HPTUDapAad

| Residue | HN  | Hα  | Hβ   | Others                                      |
|---------|-----|-----|------|---------------------------------------------|
| Ac      |     |     | 2.039|                                             |
| Arg1    | 8.365| 4.336| 1.756, 1.843 | Hy: 1.628, 1.670; Hδ: 3.207; HNt: 7.216 |
| Thr2    | 8.264| 4.405| 4.204 | Hy: 1.193                                    |
| Val3    | 8.237| 4.171| 2.075 | Hy: 0.932                                    |
| Dap4a   | 8.873| 4.805| 3.256, 3.429 |                                            |
| Val5    | 8.455| 4.452| 2.098 | Hy: 0.915, 0.982                             |
| Pro6    |     | 4.412| 1.937, 2.318 | Hy: 2.001, 2.078; Hδ: 3.697, 3.883 |
| Gly7    | 8.479| 3.927, 3.997 |                                            |
| Orn8    | 8.234| 4.391| 1.878 | Hy: 1.707, 1.751; Hδ: 3.011;                 |
| Aad9c   | 8.406| 4.288| 1.704, 1.751 | Hy: 1.535, 1.619; Hδ: 2.205, 2.245 |
| Ile10d  | 8.269| 4.122| 1.840 | Hy: 1.185, 1.489, 0.882 (Me); Hδ: 0.851 |
| Leu11   | 8.356| 4.376| 1.648 | Hy: 1.574; Hδ: 0.860, 0.923                  |
| Gln12   | 8.379| 4.288| 1.975, 2.112 | Hy: 2.352, 2.381; HNt: 6.875, 7.555 |
| NH₂     |     |     | 7.114, 7.595 |                                            |

aSignal for the terminal HN not observed; bThe assignments for the minor Gly7 spin system are 8.638(HN), 3.893, 4.022(Hα); cAad9 spin system are 8.450(HN), 4.281(Hα), 1.721(Hβ), 1.536, 1.624(Hγ); dIle10 spin system are 8.313(HN), 4.131(Hα), 1.834(Hβ), 1.190, 1.484(Hγ); 0.879(Me(Hγ)); 0.879(Hδ).

Table S30. The $^1$H Chemical Shift Assignments for Peptide HPTUDabAad

| Residue | HN  | Hα  | Hβ   | Others                                      |
|---------|-----|-----|------|---------------------------------------------|
| Ac      |     |     | 2.040|                                             |
| Arg1    | 8.353| 4.338| 1.748, 1.835 | Hy: 1.619, 1.665; Hδ: 3.203; HNt: 7.215 |
| Thr2    | 8.258| 4.377| 4.178 | Hy: 1.184                                    |
| Val3    | 8.213| 4.116| 2.044 | Hy: 0.919                                    |
| Dab4ab  | 8.657| 4.509| 3.009, 3.054 | Hy: 2.048, 2.116;                             |
| Val5c   | 8.403| 4.426| 2.086 | Hy: 0.933, 0.980                             |
| Pro6    |     | 4.406| 1.964, 2.314 | Hy: 2.072; Hδ: 3.702, 3.879 |
| Gly7d   | 8.457| 3.923, 3.999 |                                            |
| Orn8    | 8.244| 4.387| 1.875 | Hy: 1.707, 1.761; Hδ: 3.011; HNt: 7.627     |
| Aad9e   | 8.407| 4.289| 1.704, 1.751 | Hy: 1.541, 1.618; Hδ: 2.216, 2.255 |
| Ile10f  | 8.274| 4.123| 1.838 | Hy: 1.486, 1.184, 0.881 (Me); Hδ: 0.848 |
| Leu11   | 8.354| 4.375| 1.648 | Hy: 1.571; Hδ: 0.857, 0.924                  |
| Gln12   | 8.376| 4.288| 1.976, 2.109 | Hy: 2.353, 2.380; HNt: 6.875, 7.554 |
| NH₂     |     |     | 7.114, 7.595 |                                            |

aSignal for the terminal HN not observed. bThe assignments for the minor Dab4 spin system are 8.602(HN), 4.483(Hα), 3.040(Hβ), 2.039, 2.130(Hγ); cVal5 spin system are 8.158(HN), 4.246(Hα), 1.997(Hβ), 0.901(Hγ); dGly7 spin system are 8.662(HN), 3.882, 4.034(Hα); eAad9 spin system are 8.450(HN), 4.280(Hα), 1.718(Hβ), 1.536, 1.620(Hγ), 2.232(Hδ); fIle10 spin system are 8.311(HN), 4.129(Hα), 1.833(Hβ), 1.482, 1.182(Hγ), 0.879(Me(Hγ)).
### Table S31. The $^1$H Chemical Shift Assignments for Peptide HPTUO

| Residue | HN   | Ha   | Hβ   | Others                      |
|---------|------|------|------|----------------------------|
| Ac-     | 2.039|      |      |                            |
| Arg1    | 8.347| 4.341| 1.750, 1.834 | Hγ: 1.619, 1.663; Hδ: 3.204; HNt: 7.215 |
| Thr2    | 8.266| 4.375| 4.171 | Hγ: 1.183                  |
| Val3$^b$| 8.206| 4.112| 2.041 | Hγ: 0.917                  |
| Orn4$^{a,c}$ | 8.513| 4.396| 1.815 | Hγ: 1.654, 1.739; Hδ: 3.007 |
| Val5    | 8.360| 4.425|      | Hγ: 0.937, 0.978           |
| Pro6    |      | 4.403| 1.939, 2.317 | Hγ: 1.998, 2.072; Hδ: 3.701, 3.879 |
| Gly7    | 8.447| 3.922| 4.003|                            |
| Orn8    | 8.248| 4.337| 1.877 | Hγ: 1.697, 1.757 ; Hδ: 3.011; HNt: 7.624 |
| Aad9    | 8.414| 4.289| 1.706, 1.745 | Hγ: 1.536, 1.624; Hδ: 2.214, 2.253 |
| Ile10   | 8.278| 4.122| 1.840 | Hγ: 1.493, 1.184, 0.881 (Me); Hδ: 0.853 |
| Leu11   | 8.356| 4.376| 1.648 | Hγ: 1.574; Hδ: 0.862, 0.924 |
| Gln12   | 8.380| 4.289| 1.971, 2.113 | Hγ: 2.352, 2.382; HNt: 6.874, 7.555 |
| NH$_2$  | 7.115|      |      |                            |

$^a$Signal for the terminal HN not observed; $^b$The assignments for the minor Val3 spin system are 8.094(HN), 4.250(Ha), 1.994(Hβ), 0.900(Hγ); $^c$Orn4 spin system are 8.464(HN), 4.370(Ha), 1.829(Hβ), 1.662, 1.737(Hγ), 3.009(Hδ).

### Table S32. The $^1$H Chemical Shift Assignments for Peptide HPTULysAad

| Residue | HN   | Ha   | Hβ   | Others                      |
|---------|------|------|------|----------------------------|
| Ac-     | 2.042|      |      |                            |
| Arg1    | 8.327| 4.343| 1.748, 1.883 | Hγ: 1.618, 1.659; Hδ: 3.204; HNt: 7.208 |
| Thr2    | 8.257| 4.369| 4.165 | Hγ: 0.923                  |
| Val3$^a$| 8.183| 4.116| 2.039 | Hγ: 0.912                  |
| Lys4    | 8.424| 4.349| 1.759 | Hγ: 1.343, 1.417; Hδ: 1.719; He: 2.976; HNt: 7.541 |
| Val5    | 8.285| 4.423| 2.072 | Hγ: 0.932, 0.967           |
| Pro6    |      | 4.392| 1.945, 2.310 | Hγ: 1.985, 2.069; Hδ: 3.701, 3.879 |
| Gly7    | 8.437| 3.926| 3.994|                            |
| Orn8    | 8.228| 4.391| 1.880 | Hγ: 1.710, 1.768 ; Hδ: 3.013; HNt: 7.617 |
| Aad9    | 8.395| 4.292| 1.706, 1.752 | Hγ: 1.535, 1.623; Hδ: 2.210, 2.247 |
| Ile10   | 8.252| 4.126| 1.840 | Hγ: 1.477, 1.180, 0.881 (Me); Hδ: 0.855 |
| Leu11   | 8.334| 4.375| 1.649 | Hγ: 1.574; Hδ: 0.863, 0.922 |
| Gln12   | 8.357| 4.292| 1.974, 2.112 | Hγ: 2.355, 2.375; HNt: 6.874, 7.555 |
| NH$_2$  | 7.102|      |      |                            |

$^a$The assignments for the minor Val3 spin system are 7.984(HN), 4.257(Ha), 1.994(Hβ), 0.905(Hγ).
### Table S33. The $^1$H Chemical Shift Assignments for Peptide HPTFDapAad

| Residue | HN   | Hα          | Hβ          | Others                                           |
|---------|------|-------------|-------------|-------------------------------------------------|
| Ac-     | 2.082|             |             |                                                 |
| Cys1    | 8.450| 5.220       | 2.661, 3.168|                                                 |
| Arg2    | 8.765| 4.690       | 1.840       | Hγ: 1.547, 1.683; Hδ: 3.186; HNt: 7.316         |
| Thr3    | 8.583| 4.974       | 3.946       | Hγ: 1.085                                       |
| Val4    | 9.161| 4.502       | 2.035       | Hγ: 0.849, 0.874                               |
| Dap5    | 8.911| 5.299       | 3.310, 3.390|                                                 |
| Val6    | 8.780| 4.632       | 1.936       | Hγ: 0.870, 0.901                               |
| DPro7   | 4.368| 1.969, 2.367|             | Hγ: 2.044, 2.106; Hδ: 3.776, 3.850              |
| Gly8    | 8.783| 3.859, 3.999|             |                                                 |
| Orn9    | 7.946| 4.673       | 1.845       | Hγ: 1.701; Hδ: 3.007; HNt: 7.618                |
| Aad10   | 8.513| 4.960       | 1.583, 1.705| Hγ: 1.400, 1.522; Hδ: 2.099                    |
| Ile11   | 8.899| 4.491       | 1.809       | Hγ: 1.096, 1.323, 0.845 (Me); Hδ: 0.785         |
| Leu12   | 8.479| 4.708       | 1.667       | Hγ: 1.493; Hδ: 0.781, 0.820                     |
| Gln13   | 9.205| 4.643       | 1.857, 2.074| Hγ: 2.210, 2.267; HNt: 6.822, 7.334            |
| Cys14   | 8.991| 5.085       | 3.066, 3.133|                                                 |
| NH$_2$  | 7.242| 7.607       |             |                                                 |

*aSignal for the terminal HN not observed.

### Table S34. The $^1$H Chemical Shift Assignments for Peptide HPTFDabAad

| Residue | HN   | Hα          | Hβ          | Others                                           |
|---------|------|-------------|-------------|-------------------------------------------------|
| Ac-     | 2.082|             |             |                                                 |
| Cys1    | 8.449| 5.223       | 2.654, 3.170|                                                 |
| Arg2    | 8.763| 4.693       | 1.842       | Hγ: 1.542, 1.688; Hδ: 3.185 HNt: 7.128          |
| Thr3    | 8.594| 4.976       | 3.945       | Hγ: 1.080                                       |
| Val4    | 9.103| 4.460       | 1.988       | Hγ: 0.814, 0.855                               |
| Dab5    | 8.747| 5.172       | 2.013, 2.122| Hγ: 2.910, 2.942                               |
| Val6    | 8.619| 4.604       | 1.918       | Hγ: 0.874, 0.903                               |
| DPro7   | 4.378| 1.968, 2.348|             | Hγ: 2.041, 2.134; Hδ: 3.754, 3.867              |
| Gly8    | 8.768| 3.905, 3.992|             |                                                 |
| Orn9    | 7.940| 4.711       | 1.847       | Hγ: 1.703 ; Hδ: 3.013; HNt: 7.623               |
| Aad10   | 8.575| 4.926       | 1.602, 1.694| Hγ: 1.373, 1.499; Hδ: 2.082, 2.102              |
| Ile11   | 9.019| 4.497       | 1.823       | Hγ: 1.083, 1.328, 0.850 (Me); Hδ: 0.795         |
| Leu12   | 8.448| 4.713       | 1.661       | Hγ: 1.488; Hδ: 0.782, 0.817                     |
| Gln13   | 9.215| 4.663       | 1.877, 2.075| Hγ: 2.210, 2.269; HNt: 6.863, 7.544             |
| Cys14   | 8.990| 5.085       | 3.066, 3.131|                                                 |
| NH$_2$  | 7.240| 7.606       |             |                                                 |

*aSignal for the terminal HN not observed.*
Table S35. The $^1$H Chemical Shift Assignments for Peptide HPTFOrN Aad

| Residue | HN   | Hα   | Hβ    | Others                          |
|---------|------|------|-------|---------------------------------|
| Ac-     | 2.078|      |       |                                 |
| Cys     | 8.455| 5.221| 2.643 | 3.169                           |
| Arg1    | 8.760| 4.687| 1.841 | Hγ: 1.539, 1.684; Hδ: 3.186; HNt: 7.125 |
| Thr2    | 8.585| 4.985| 3.939 | Hγ: 1.076                       |
| Val3    | 9.102| 4.434| 1.969 | Hγ: 0.815                       |
| Orn4    | 8.555| 4.951| 1.711 | Hγ: 1.554, 1.622; Hδ: 2.916      |
| Val5    | 8.827| 4.577| 1.936 | Hγ: 0.885                       |
| D-Pro6  | 4.375|      | 1.970 | Hγ: 2.035, 2.137; Hδ: 3.731, 3.864|
| Gly7    | 8.729|      | 3.930 |                                 |
| Orn8    | 7.938| 4.710| 1.835 | Hγ: 1.695; Hδ: 3.009; HNt: 7.614 |
| Aad9    | 8.507| 4.909| 1.587 | Hγ: 2.081; Hδ: 1.358, 1.486     |
| Ile10   | 9.084| 4.493| 1.842 | Hγ: 1.108, 1.330, 0.852(Me); Hδ: 0.785 |
| Leu11   | 8.434| 4.710| 1.846 | Hγ: 1.657; Hδ: 0.781, 0.815     |
| Gln12   | 9.219| 4.660| 2.214 | Hγ: 1.875, 2.074; HNt: 6.829, 7.316 |
| Cys     | 8.995| 5.086| 3.001 |                                 |
| NH2     | 7.242| 7.605|       |                                 |

$^a$Signal for the terminal HN not observed.

Table S36. The $^1$H Chemical Shift Assignments for Peptide HPTF Lys Aad

| Residue | HN   | Hα   | Hβ    | Others                          |
|---------|------|------|-------|---------------------------------|
| Ac-     | 2.079|      |       |                                 |
| Cys     | 8.445| 5.221| 2.655 | 3.168                           |
| Arg1    | 8.763| 4.674| 1.841 | Hγ: 1.538, 1.687; Hδ: 3.182 HNt: 7.127 |
| Thr2    | 8.577| 4.991| 3.941 | Hγ: 1.079                       |
| Val3    | 9.067| 4.430| 1.975 | Hγ: 0.811, 0.850                |
| Lys4    | 8.470| 4.957| 1.599 | Hγ: 1.193, 1.250; Hδ: 2.859, 2.899 |
| Val5    | 8.805| 4.580| 1.937 | Hγ: 0.880, 0.908                |
| D-Pro6  | 4.364|      | 1.959 | Hγ: 2.040, 2.141; Hδ: 3.776, 3.861 |
| Gly7    | 8.666| 3.842| 3.974 |                                 |
| Orn8    | 7.933| 4.694| 1.807 | Hγ: 1.686; Hδ: 3.008; HNt: 7.618 |
| Aad9    | 8.545| 4.809| 1.598 | Hγ: 1.373, 1.487; Hδ: 2.073, 2.112 |
| Ile10   | 9.139| 4.479| 1.850 | Hγ: 1.128, 1.343, 0.851 (Me); Hδ: 0.787 |
| Leu11   | 8.403| 4.714| 1.657 | Hγ: 1.485; Hδ: 0.782, 0.817     |
| Gln12   | 9.213| 4.664| 1.879 | Hγ: 2.210, 2.268; HNt: 6.826, 7.312 |
| Cys     | 8.981| 5.084| 2.999 | 3.132                           |
| NH2     | 7.238| 7.606|       |                                 |

$^a$Signal for the terminal HN not observed.
### Table S37. The $^3J_{HN\alpha}$ (Hz) Values of the HPTXaaAsp Peptides

| Residue | Xaa | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|-----|
| Arg1    | 10  | 10  | 10  | 8.8 |
| Thr2    | 11  | 11  | 8.8 | 10  |
| Val3    | 9.4 | 10  | 11  | 8.8 |
| **Xaa4**| 11  | 11  | 13  | 11  |
| Val5    | 10  | 12  | 8.9 | 11  |
| Gly7    | 10  | 9.2 | 10  | 10  |
| Orn8    | 12  | 11  | 7.6 | 10  |
| **Asp9**| 9.2 | 11  | 10  | 11  |
| Ile10   | 9.2 | 11  | 8.8 | 11  |
| Leu11   | 12  | 11  | 10  | 8.8 |
| Gln12   | 10  | 10  | 10  | 10  |

### Table S38. The $^3J_{HN\alpha}$ (Hz) Values of the HPTXaaGlu Peptides

| Residue | Xaa | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|-----|
| Arg1    | 8.8 | 8.8 | 10  | 8.6 |
| Thr2    | 11  | 10  | 11  | 11  |
| Val3    | 9.9 | 9.8 | 10  | 8.4 |
| **Xaa4**| 11  | 10  | 10  | 10  |
| Val5    | 10  | 9.4 | 10  | 10  |
| Gly7    | 8.4 | 8.8 | 12  | 8.8 |
| Orn8    | 10  | 10  | 10  | 10  |
| **Glu9**| 9.2 | 9.6 | 10  | 10  |
| Ile10   | 9.0 | 11  | 11  | 11  |
| Leu11   | 8.8 | 9.9 | 8.6 | 10  |
| Gln12   | 8.6 | 9.0 | 7.7 | 8.6 |
### Table S39. The $^3J_{\text{HNN}}$ (Hz) Values of the HPTXaaAad Peptides.

| Residue | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|
| Arg1    | 11  | 10  | 9.9 | 8.8 |
| Thr2    | 11  | 11  | 10  | 11  |
| Val3    | 11  | 10  | 8.6 | 10  |
| **Xaa4** | 12  | 10  | 11  | 8.1 |
| Val5    | 12  | 11  | 11  | 11  |
| Gly7    | 11  | 11  | 14  | 9.0 |
| Orn8    | 11  | 11  | 10  | 11  |
| **Aad9** | 11  | 11  | 11  | 9.9 |
| Ile10   | 10  | 10  | 11  | 9.4 |
| Leu11   | 10  | 10  | 9.8 | 9.9 |
| Gln12   | 9.0 | 10  | 8.4 | 9.8 |

### Table S40. The $^3J_{\text{HNN}}$ (Hz) Values of the HPTUXaaAsp Peptides.

| Residue | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|
| Arg1    | 9.8 | 9.8 | 8.8 | 8.6 |
| Thr2    | 9.2 | 10  | 11  | 11  |
| Val3    | 8.6 | 10  | 9.2 | 9.6 |
| **Xaa4** | 12  | 12  | 10  | 10  |
| Val5    | 11  | 9.8 | 9.4 | 11  |
| Gly7    | 6.8 | 7.7 | 15  | 7.9 |
| Orn8    | 11  | 11  | 9.8 | 9.9 |
| **Asp9** | 9.8 | 9.4 | 9.8 | 9.8 |
| Ile10   | 10  | 8.8 | 10  | 10  |
| Leu11   | 10  | 9.2 | 9.8 | 9.9 |
| Gln12   | 8.8 | 11  | 11  | 11  |
**Table S41.** The \(^3J_{HNa}\) (Hz) Values of the HPTUXaaGlu Peptides.

| Residue | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|
| Arg1    | 9.4 | 10  | 9.2 | 9.0 |
| Thr2    | 12  | 9.0 | 8.8 | 9.4 |
| Val3    | 10  | 9.8 | 9.8 | 9.8 |
| **Xaa4**| 14  | 7.7 | 11  | 10  |
| Val5    | 11  | 9.6 | 9.9 | 9.8 |
| Gly7    | 15  | 9.8 | 9.0 | 8.8 |
| Orn8    | 10  | 8.1 | 9.4 | 9.4 |
| **Glu9**| 9.9 | 9.9 | 8.6 | 8.8 |
| Ile10   | 11  | 11  | 10  | 11  |
| Leu11   | 9.9 | 8.2 | 9.9 | 9.9 |
| Gln12   | 10  | 9.8 | 7.7 | 9.8 |

**Table S42.** The \(^3J_{HNa}\) (Hz) Values of the HPTUXaaAad Peptides.

| Residue | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|
| Arg1    | 9.9 | 9.2 | 10  | 9.3 |
| Thr2    | 13  | 7.3 | 10  | 10  |
| Val3    | 9.8 | 11  | 11  | 10  |
| **Xaa4**| 12  | 11  | 10  | 9.0 |
| Val5    | 8.9 | 11  | 9.9 | 9.8 |
| Gly7    | 8.8 | 10  | 10  | 9.0 |
| Orn8    | 9.6 | 9.0 | 8.8 | 9.6 |
| **Aad9**| 7.9 | 8.6 | 10  | 10  |
| Ile10   | 10  | 10  | 10  | 11  |
| Leu11   | 8.6 | 11  | 8.6 | 10  |
| Gln12   | 9.4 | 10  | 8.8 | 9.9 |
**Table S43.** The $^3J_{HN\alpha}$(Hz) Values of the HPTFXaaAsp Peptides.

| Residue | Xaa | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|-----|
| Cys     |     | 9.4 | 11  | 10  | 10  |
| Arg1    |     | 12  | 8.4 | 11  | 11  |
| Thr2    |     | 11  | 11  | 11  | 11  |
| Val3    |     | 10  | 12  | 11  | 11  |
| **Xaa4**|     | 11  | 10  | 13  | 12  |
| Val5    |     | 12  | 10  | 11  | 12  |
| Gly7    |     | 8.1 | 10  | 11  | 5   |
| Orn8    |     | 12  | 10  | 11  | 11  |
| **Asp9**|     | 11  | 8.4 | 11  | 11  |
| Ile110  |     | 10  | 11  | 11  | 10  |
| Leu11   |     | 11  | 11  | 11  | 10  |
| Gln12   |     | 11  | 11  | 11  | 10  |
| Cys     |     | 11  | 11  | 11  | 12  |

**Table S44.** The $^3J_{HN\alpha}$(Hz) Values of the HPTFXaaGlu Peptides.

| Residue | Xaa | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|-----|
| Cys     |     | 11  | 11  | 10  | 11  |
| Arg1    |     | 10  | 11  | 11  | 9.6 |
| Thr2    |     | 11  | 10  | 9.4 | 11  |
| Val3    |     | 11  | 12  | 11  | 12  |
| **Xaa4**|     | 12  | 12  | 11  | 12  |
| Val5    |     | 11  | 10  | 11  | 11  |
| Gly7    |     | 9.2 | 10  | 14  | 8.1 |
| Orn8    |     | 10  | 11  | 11  | 12  |
| **Glu9**|     | 10  | 10  | 10  | 11  |
| Ile110  |     | 11  | 11  | 11  | 11  |
| Leu11   |     | 9.4 | 9.6 | 10  | 11  |
| Gln12   |     | 10  | 12  | 11  | 10  |
| Cys     |     | 10  | 11  | 11  | 12  |
Table S45. The $^3J_{HNa}$ (Hz) Values of the HPTFXaaAad Peptides.

| Residue | Dap | Dab | Orn | Lys |
|---------|-----|-----|-----|-----|
| Cys     | 12  | 10  | 10  | 10  |
| Arg1    | 11  | 9.2 | 11  | 9.4 |
| Thr2    | 12  | 10  | 10  | 11  |
| Val3    | 11  | 10  | 10  | 11  |
| **Xaa4** | 11  | 9.6 | 9.2 | 10  |
| Val5    | 10  | 11  | 10  | 11  |
| Gly7    | 12  | 10  | 14  | 8.3 |
| Orn8    | 12  | 11  | 11  | 11  |
| **Aad9** | 11  | 8.9 | 11  | 11  |
| Ile110  | 12  | 12  | 10  | 12  |
| Leu11   | 9.4 | 9.9 | 10  | 11  |
| Gln12   | 13  | 11  | 10  | 10  |
| Cys     | 10  | 12  | 11  | 11  |
Figure S1. The Hα chemical shift deviation for the residues in the experimental HPTXaaZbb peptides: HPTDapAsp (a), HPTDapGlu (b), HPTDapAad (c), HPTDabAsp (d), HPTDabGlu (e), HPTDabAad (f), HPTOrnAsp (g), HPTOrnGlu (h), HPTOrnAad (i), HPTLysAsp (j), HPTLysGlu (k), HPTLysAad (l).
Figure S2. The Hα chemical shift deviation for the residues in the fully folded reference HPTFxaaZbb peptides: HPTFDapAsp (a), HPTFDapGlu (b), HPTFDapAad (c), HPTFDabAsp (d), HPTFDabGlu (e), HPTFDabAad (f), HPTFOrnAsp (g), HPTFOrnGlu (h), HPTFOrnAad (i), HPTFLysAsp (j), HPTFLysGlu (k), HPTFLysAad (l).
Figure S3. The NOEs in the ROESY spectra of HPTDapAsp involving side chain protons.

Figure S4. The NOEs in the ROESY spectra of HPTFDapAsp involving side chain protons.

Figure S5. The NOEs in the ROESY spectra of HPTUDapAsp involving side chain protons.
Figure S6. The NOEs in the ROESY spectra of HPTDabAsp involving side chain protons.

Figure S7. The NOEs in the ROESY spectra of HPTFDabAsp involving side chain protons.

Figure S8. The NOEs in the ROESY spectra of HPTUDabAsp involving side chain protons.
Figure S9. The NOEs in the ROESY spectra of HPTOrnAsp involving side chain protons.

Figure S10. The NOEs in the ROESY spectra of HPTFOrnAsp involving side chain protons.

Figure S11. The NOEs in the ROESY spectra of HPTUOrnAsp involving side chain protons.
Figure S12. The NOEs in the ROESY spectra of HPTLysAsp involving side chain protons.

Figure S13. The NOEs in the ROESY spectra of HPTFLysAsp involving side chain protons.

Figure S14. The NOEs in the ROESY spectra of HPTULysAsp involving side chain protons.
Figure S15. The NOEs in the ROESY spectra of HPTDapGlu involving side chain protons.

Figure S16. The NOEs in the ROESY spectra of HPTFDapGlu involving side chain protons.

Figure S17. The NOEs in the ROESY spectra of HPTUDapGlu involving side chain protons.
**Figure S18.** The NOEs in the ROESY spectra of HPTDabGlu involving side chain protons.

**Figure S19.** The NOEs in the ROESY spectra of HPTFDabGlu involving side chain protons.

**Figure S20.** The NOEs in the ROESY spectra of HPTDabGlu involving side chain protons.
Figure S21. The NOEs in the ROESY spectra of HPTOrnGlu involving side chain protons.

Figure S22. The NOEs in the ROESY spectra of HPTFOrnGlu involving side chain protons.

Figure S23. The NOEs in the ROESY spectra of HPTUOrnGlu involving side chain protons.
**Figure S24.** The NOEs in the ROESY spectra of HPTLysGlu involving side chain protons.

**Figure S25.** The NOEs in the ROESY spectra of HPTFLysGlu involving side chain protons.

**Figure S26.** The NOEs in the ROESY spectra of HPTULysGlu involving side chain protons.
**Figure S27.** The NOEs in the ROESY spectra of HPTDapAad involving side chain protons.

**Figure S28.** The NOEs in the ROESY spectra of HPTFDapAad involving side chain protons.

**Figure S29.** The NOEs in the ROESY spectra of HPTUDapAad involving side chain protons.
**Figure S30.** The NOEs in the ROESY spectra of HPTDabAad involving side chain protons.

**Figure S31.** The NOEs in the ROESY spectra of HPTFDabAad involving side chain protons.

**Figure S32.** The NOEs in the ROESY spectra of HPTUDabAad involving side chain protons.
**Figure S33.** The NOEs in the ROESY spectra of HPTOrnAad involving side chain protons.

**Figure S34.** The NOEs in the ROESY spectra of HPTFOrnAad involving side chain protons.

**Figure S35.** The NOEs in the ROESY spectra of HPTUOrnAad involving side chain protons.
Figure S36. The NOEs in the ROESY spectra of HPTLysAad involving side chain protons.

Figure S37. The NOEs in the ROESY spectra of HPTFLysAad involving side chain protons.

Figure S38. The NOEs in the ROESY spectra of HPTULysAad involving side chain protons.
Figure S39. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDapAsp (a), HPTFDapAsp (b), and HPTUDapAsp (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S40. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDabAsp (a), HPTFDabAsp (b), and HPTUDabAsp (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S41. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTOrnAsp (a), HPTFOrnAsp (b), and HPTUOrnAsp (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S42. Wüthrich diagrams of the backbone NOE connectivities involving the $\alpha$-protons and amide protons for peptides HPTLysAsp (a), HPTFLysAsp (b), and HPTULysAsp (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S43. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDapGlu (a), HPTFDapGlu (b), and HPTUDapGlu (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S44. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDabGlu (a), HPTFDabGlu (b), and HPTUDabGlu (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S45. Wüthrich diagrams of the backbone NOE connectivities involving the $\alpha$-protons and amide protons for peptides HPTOrnGlu (a), HPTFOrnGlu (b), and HPTUDrnGlu (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S46. Wüthrich diagrams of the backbone NOE connectivities involving the $\alpha$-protons and amide protons for peptides HPTLysGlu (a), HPTFLysGlu (b), and HPTULysGlu (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S47. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDapAad (a), HPTFDapAad (b), and HPTUDapAad (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S48. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTDabAad (a), HPTFDabAad (b), and HPTUDabAad (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S49. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTOrnAad (a), HPTFOrnAad (b), and HPTUOrnAad (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S50. Wüthrich diagrams of the backbone NOE connectivities involving the α-protons and amide protons for peptides HPTLysAad (a), HPTFLysAad (b), and HPTULysAad (c). The line thickness reflects the NOE intensity and interproton distance; the thicker the line, the stronger the NOE intensity, the shorter the distance.
Figure S51. The fraction folded of the residues in HPTXaaZbb peptides. HPTDapAsp (a), HPTDapGlu (b), HPTDapAad (c), HPTDabAsp (d), HPTDabGlu (e), HPTDabAad (f), HPTOrnAsp (g), HPTOrnGlu (h), HPTOrnAad (i), HPTLysAsp (j), HPTLysGlu (k), HPTLysAad (l).
Figure S52. The $\Delta G_{\text{fold}}$ of the residues in HPTXaaZbb peptides. HPTDapAsp (a), HPTDapGlu (b), HPTDapAad (c), HPTDabAsp (d), HPTDabGlu (e), HPTDabAad (f), HPTOrnAsp (g), HPTOrnGlu (h), HPTOrnAad (i), HPTLysAsp (j), HPTLysGlu (k), HPTLysAad (l).
Figure S53. The low energy conformations for peptide HPTAadDab from the side chain conformational analysis by molecular mechanics calculations.
Figure S54. The low energy conformations for peptide HPTDabAad from the side chain conformational analysis by molecular mechanics calculations.
Material and Methods

General Section

All reagents and solvents were used without purification. Diisopropylethylamine (DIEA), piperidine, trifluoroacetic acid (TFA), acetic anhydride (Ac₂O) were purchased from Acros. Nα-Fmoc-Nβ-Boc-L-2,3-diaminopropionic acid, Nα-Fmoc-Nγ-Boc-L-2,4-diaminobutyric acid, Nα-Fmoc-D-proline, dimethylformamide (DMF), methanol, and acetonitrile were purchased from Merck. Nα-Fmoc-aminoacidipic acid-δ-t-butyl ester was from BaChem. Nα-Fmoc-amino acids, 1-hydroxybenzotriazole (HOBt), 2-(1H-Benzotriazole-1-yl)-1, 3, 3-tetramethylyluronium hexafluorophosphate (HBTU), NovaSyn® TGR resin were from NovaBiochem. Hexanes were from Duksan. Analytical reverse phase (RP)-HPLC was performed on an Agilent 1200 series chromatography system using a Vydac C₁₈ column (4.6 mm diameter, 250 mm length). Preparative RP-HPLC was performed on Waters Breeze chromatography system using a Seppak® plus short tC₁₈ cartridges, Vydac C₄ or C₁₈ column (22 mm diameter, 250 mm length) Mass spectrometry of the peptides was performed on a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) (Bruker BIFLEX) using α-cyano-4-hydroxycinnamic acid as the matrix. 2-Dimensional nuclear magnetic resonance spectroscopy experiments were performed on the Bruker AV III 800MHz spectrometer.

Peptide Synthesis

The peptides were synthesized by solid phase peptide synthesis using Fmoc-based chemistry [1, 2]. NovaSyn® TGR resin (0.050 mmol) was swollen in N, N-dimethylformamide (DMF, 3 mL) for 30 minutes. A mixture of 3 equivalents of the appropriately protected Fmoc-amino acid, HOBt, and HBTU was dissolved in DMF (1 mL). Diisopropylethylamine (DIEA, 8 equivalents) was then added to the solution and mixed thoroughly. The solution was then applied to the resin. The vial that contained the solution was rinsed with DMF (5 mL, 5x1 min). The Fmoc-group was then removed by 20% piperidine/DMF (5 mL, 3x8 min). After the final residue was coupled, a solution of acetic anhydride (20 equivalents), DIEA (20 equivalents), and DMF (3 mL) was added to resin for capping. The reaction was shaken for 2 hours.

Peptides were deprotected and cleaved off the resin by treating the resin with 5 mL 95:5 trifluoroacetic acid (TFA)/triisopropylsilane and shaken for 2 hours. For Cys-containing peptides, 5 mL 90:5:5 trifluoroacetic acid (TFA)/triisopropylsilane/ethanedithiol was used instead. The solution was then filtered through glass wool and the resin was washed with TFA (3x1.5 mL). The combined filtrate was evaporated gently by an air pump (nitrogen gas was used for the Cys-containing peptides). The resulting material was washed with hexanes
(3x3 mL), dissolved in water, and lyophilized. The peptide (1 mg/mL, aqueous solution) was
analyzed using analytical RP-HPLC on a 25 cm C18 column (dia 4.6 mm) with flow rate 1
mL/min, temperature 25°C, linear 1%/min gradient from 100% A to 0% A (solvent A: 99.9% water, 0.1% TFA; solvent B: 90% acetonitrile, 10% water, 0.1% TFA). The disulfide bond of the Cys-containing HPTFXaaZbb peptides were formed via charcoal mediated air
oxidation [3]. Peptides were purified to higher than 95% purity by Sep-Pak® Plus Short tC18
 cartridges using an appropriate percentage of B solvent and by reverse phase HPLC using a
preparative C4 and C18 columns with flow rate 10 mL·min⁻¹, temperature 25°C, linear 0.5
%·min⁻¹ gradient. Appropriate linear gradients of solvent A and solvent B were used for each
peptide to place the retention time for the desired peptide between 20 and 30 minutes. These
gradients are listed individually for each peptide (vide infra); for example, PLG15_25 was
used to purify HPTDapAsp using a C18 column, representing the linear gradient from 15 % B
to 25 % B (flow rate 10 mL·min⁻¹, temperature 25°C, linear 0.5 %·min⁻¹ gradient). The
identity of the peptide was confirmed by MALDI-TOF.

**HPTDapAsp** (Ac-Arg Thr Val Dap Val D-Pro Gly Asp Ile Leu Gln-NH₂)

The peptide was synthesized using 200.2 mg (0.050 mmol) of NovaSyn® TGR resin.
The synthesis gave 286.6 mg of resin (99.2% yield). The cleavage yielded 52.6 mg of crude
peptide (87.0% yield). The peptide was purified by preparative RP-HPLC using a C4
(PLG8_18) and a C18 column (PLG15_25) to give a 10.6 mg of pure peptide (96.9% purity).
Retention time on analytical RP-HPLC was 27.4 minutes. The identity of the peptide was
confirmed by MALDI-TOF mass spectrometry. Calculated for C₅₈H₁₀₃N₁₉O₁₇ [MH]⁺: 1338.785; observed: 1338.776. The concentration of the peptide for NMR analysis was 10.5
mM.

**HPTDabAsp** (Ac-Arg Thr Val Dab Val D-Pro Gly Orn Asp Ile Leu Gln-NH₂)

The peptide was synthesized using 203.9 mg (0.051 mmol) of NovaSyn® TGR resin.
The synthesis gave 293.0 mg of resin (99.2% yield). The cleavage yielded 55.3 mg of crude
peptide (88.0% yield). The peptide was purified by preparative RP-HPLC using a C4
(PLG7_17) and a C18 column (PLG15_25) to give a 12.3 mg of pure peptide (96.1% purity).
Retention time on analytical RP-HPLC was 27.4 minutes. The identity of the peptide was
confirmed by MALDI-TOF mass spectrometry. Calculated for C₅₉H₁₀₅N₁₉O₁₇ [MH]⁺: 1352.801; observed: 1352.822. The concentration of the peptide for NMR analysis was 10.5
mM.

**HPTOrnAsp** (Ac-Arg Thr Val Orn Val D-Pro Gly Orn Asp Ile Leu Gln-NH₂)

The peptide was synthesized using 204.8 mg (0.051 mmol) of NovaSyn® TGR resin.
The synthesis gave 291.8 mg of resin (87.8% yield). The cleavage yielded 57.3 mg of crude
peptide (75.8% yield). The peptide was purified by preparative RP-HPLC using a C4 column
to give a 18.9 mg of pure peptide (95.9% purity). Retention time on analytical RP-HPLC was 27.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]^{+}: 1366.817; observed: 1367.091. The concentration of the peptide for NMR analysis was 9.9 mM.

**HPTLysAsp** (Ac-Arg Thr Val Lys Val ^D^Pro Gly Orn Asp Ile Leu Gln-NH_{2})

The peptide was synthesized using 200.0 mg (0.050 mmol) of NovaSyn^®^ TGR resin. The synthesis gave 291.6 mg of resin (>99% yield). The cleavage yielded 57.0 mg of crude peptide (83.0% yield). The peptide was purified by preparative RP-HPLC using a C4 (PLG7_17) and a C18 column (PLG16_26) to give 7.4 mg of pure peptide (96.0% purity). Retention time on analytical RP-HPLC was 27.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]^{+}: 1366.817; observed: 1367.091. The concentration of the peptide for NMR analysis was 9.9 mM.

**HPTDapGlu** (Ac-Arg Thr Val Dap Val ^D^Pro Gly Orn Glu Ile Leu Gln-NH_{2})

The peptide was synthesized using 207.3 mg (0.052 mmol) of NovaSyn^®^ TGR resin. The synthesis gave 300.1 mg of resin (93.7% yield). The cleavage yielded 52.4 mg of crude peptide (80.0% yield). The peptide was purified by preparative RP-HPLC using a C4 (PLG6_16) and a C18 column (PLG15_25) to give 9.4 mg of pure peptide (97.2% purity). Retention time on analytical RP-HPLC was 26.7 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{59}H_{105}N_{19}O_{17} [MH]^{+}: 1352.801; observed: 1352.869. The concentration of the peptide for NMR analysis was 11.0 mM.

**HPTDabGlu** (Ac-Arg Thr Val Dab Val ^D^Pro Gly Orn Glu Ile Leu Gln-NH_{2})

The peptide was synthesized using 211.0 mg (0.053 mmol) of NovaSyn^®^ TGR resin. The synthesis gave 292.4 mg of resin (98.1% yield). The cleavage yielded 48.6 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 (PLG6_16) and a C18 column (PLG15_25) to give 10.5 mg of pure peptide (95.7% purity). Retention time on analytical RP-HPLC was 26.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]^{+}: 1366.817; observed: 1366.929. The concentration of the peptide for NMR analysis was 15.4 mM.

**HPTOrnGlu** (Ac-Arg Thr Val Orn Val ^D^Pro Gly Orn Glu Ile Leu Gln-NH_{2})

The peptide was synthesized using 200.5 mg (0.050 mmol) of NovaSyn^®^ TGR resin. The synthesis gave 293.4 mg of resin (99.6% yield). The cleavage yielded 52.8 mg of crude peptide (88.0% yield). The peptide was purified by preparative RP-HPLC using a C4
(PLG8_18) and a C18 column (PLG15_25) to give 9.1 mg of pure peptide (95.9% purity). Retention time on analytical RP-HPLC was 27.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{61}H_{109}N_{19}O_{17} [MH]^+: 1380.832; observed: 1381.082. The concentration of the peptide for NMR analysis was 13.2 mM.

**HPTLysGlu** (Ac-Arg Thr Val Lys Val DPro Gly Orn Glu Leu Gln-NH$_2$)

The peptide was synthesized using 207.2 mg (0.052 mmol) of NovaSyn® TGR resin. The synthesis gave 303.3 mg of resin (99.5% yield). The cleavage yielded 52.0 mg of crude peptide (76.0% yield). The peptide was purified by preparative RP-HPLC using a C4 (PLG5_15) and a C18 column (PLG15_25) to give 9.1 mg of pure peptide (95.9% purity). Retention time on analytical RP-HPLC was 27.6 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{111}N_{19}O_{17} [MH]^+: 1394.848; observed: 1395.096. The concentration of the peptide for NMR analysis was 10.1 mM.

**HPTDapAad** (Ac-Arg Thr Val Dap Val DPro Gly Orn Aad Leu Gln-NH$_2$)

The peptide was synthesized using 200.9 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 277.9 mg of resin (73.3% yield). The cleavage yielded 30.6 mg of crude peptide (51.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC$_{18}$ cartridges (35% B) and a C18 column (PLG17_27) to 96.0% purity (15.1 mg). Retention time on analytical RP-HPLC was 27.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C$_{60}$H$_{107}$N$_{19}$O$_{17}$ [MH]$^+$: 1366.817; observed: 1366.754. The concentration of the peptide for NMR analysis was 10.0 mM.

**HPTDabAad** (Ac-Arg Thr Val Dab Val DPro Gly Orn Aad Leu Gln-NH$_2$)

The peptide was synthesized using 200.5 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 270.8 mg of resin (72.0% yield). The cleavage yielded 33.2 mg of crude peptide (56.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC$_{18}$ cartridges (35% B) and a C18 column (PLG17_27) to 96.5% purity (11.3 mg). Retention time on analytical RP-HPLC was 27.6 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C$_{61}$H$_{109}$N$_{19}$O$_{17}$ [MH]$^+$: 1380.832; observed: 1380.825. The concentration of the peptide for NMR analysis was 10.0 mM.

**HPTOrnAad** (Ac-Arg Thr Val Orn Val DPro Gly Orn Aad Leu Gln-NH$_2$)

The peptide was synthesized using 200.8 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 271.5 mg of resin (71.8% yield). The cleavage yielded 37.3 mg of crude
The peptide (62.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC<sub>18</sub> cartridges (35% B) and a C4 column (PLG6_16) to give 8.0 mg of pure peptide (97.4% purity). Retention time on analytical RP-HPLC was 28.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C<sub>62</sub>H<sub>111</sub>N<sub>19</sub>O<sub>17</sub> [MH]+: 1394.848; observed: 1395.037. The concentration of the peptide for NMR analysis was 10.4 mM.

**HPTLysAad** (Ac-Arg Thr Val Lys Val<sup>D</sup>Pro Gly Orn Aad Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 211.1 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 301.9 mg of resin (86.3% yield). The cleavage yielded 58.2 mg of crude peptide (81.5% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC<sub>18</sub> cartridges (40% B) and a C18 column (PLG17_27) to give 26.5 mg of pure peptide (97.4% purity). Retention time on analytical RP-HPLC was 27.4 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C<sub>63</sub>H<sub>113</sub>N<sub>19</sub>O<sub>17</sub> [MH]+: 1408.863; observed: 1409.219. The concentration of the peptide for NMR analysis was 10.0 mM.

**HPTUDapAsp** (Ac-Arg Thr Val Dip Val<sup>L</sup>Pro Gly Orn Asp Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 202.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 299.5 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC<sub>18</sub> cartridges (25% B) and a C18 column (PLG16_26) to give 4.4 mg of pure peptide (96.9% purity). Retention time on analytical RP-HPLC was 27.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C<sub>58</sub>H<sub>103</sub>N<sub>19</sub>O<sub>17</sub> [MH]+: 1338.785; observed: 1338.740. The concentration of the peptide for NMR analysis was 9.1 mM.

**HPTUDabAsp** (Ac-Arg Thr Val Dip Val<sup>L</sup>Pro Gly Orn Asp Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 207.6 mg (0.052 mmol) of NovaSyn TGR® resin. The synthesis gave 304.8 mg of resin (99.8% yield). The cleavage yielded 82.3 mg of crude peptide (96.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC<sub>18</sub> cartridges (25% B) and a C18 column (PLG16_26) to give 4.3 mg of pure peptide (95.7% purity). Retention time on analytical RP-HPLC was 28.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C<sub>59</sub>H<sub>105</sub>N<sub>19</sub>O<sub>17</sub> [MH]+: 1352.801; observed: 1352.826. The concentration of the peptide for NMR analysis was 9.3 mM.

**HPTUOrnAsp** (Ac-Arg Thr Val Orn Val<sup>L</sup>Pro Gly Orn Asp Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 206.8 mg (0.052 mmol) of NovaSyn® TGR resin. The synthesis gave 303.2 mg of resin (99.8% yield). The cleavage yielded 82.2 mg of crude peptide (96.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC<sub>18</sub> cartridges (25% B) and a C18 column (PLG16_26) to give 4.3 mg of pure peptide (95.7% purity). Retention time on analytical RP-HPLC was 28.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C<sub>59</sub>H<sub>105</sub>N<sub>19</sub>O<sub>17</sub> [MH]+: 1352.801; observed: 1352.826. The concentration of the peptide for NMR analysis was 9.3 mM.
The synthesis gave 303.2 mg of resin (99.7% yield). The cleavage yielded 47.6 mg of crude peptide (56.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC18 cartridges (25% B) and a C18 column (PLG15_25) to give 3.8 mg of pure peptide (95.2% purity). Retention time on analytical RP-HPLC was 26.4 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]⁺: 1366.817; observed: 1366.801. The concentration of the peptide for NMR analysis is 9.3 mM.

**HPTULysAsp** (Ac-Arg Thr Val Lys Val ¹-Pro Gly Orn Asp Ile Leu Gln-NH₂)

The peptide was synthesized using 210.8 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 313.7 mg of resin (>99.9% yield). The cleavage yielded 60.9 mg of crude peptide (67.0% yield). The peptide was purified by preparative RP-HPLC using Seppak® plus short tC18 cartridges (25% B) and a C18 column (PLG16_26) to give 5.2 mg of pure peptide (95.0% purity). Retention time on analytical RP-HPLC was 27.7 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{61}H_{109}N_{19}O_{17} [MH]⁺: 1380.833; observed: 1366.880. The concentration of the peptide for NMR analysis was 8.0 mM.

**HPTUDapGlu** (Ac-Arg Thr Val Dap Val ¹-Pro Gly Orn Glu Ile Leu Gln-NH₂)

The peptide was synthesized using 213.8 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 303.8 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG5_15) to give 11.6 mg of pure peptide (95.7% purity). Retention time on analytical RP-HPLC was 26.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{59}H_{103}N_{19}O_{17} [MH]⁺: 1352.801; observed: 1353.004. The concentration of the peptide for NMR analysis was 10.2 mM.

**HPTUDabGlu** (Ac-Arg Thr Val Dab Val ¹-Pro Gly Orn Glu Ile Leu Gln-NH₂)

The peptide was synthesized using 211.7 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 308.1 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG15_25) to give 12.0 mg of pure peptide (96.8% purity). Retention time on analytical RP-HPLC was 26.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]⁺: 1366.817; observed: 1366.909. The concentration of the peptide for NMR analysis was 9.7 mM.

**HPTUOrnGlu** (Ac-Arg Thr Val Orn Val ¹-Pro Gly Orn Glu Ile Leu Gln-NH₂)

The peptide was synthesized using 213.1 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 312.9 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG15_25) to give 12.0 mg of pure peptide (96.8% purity). Retention time on analytical RP-HPLC was 26.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17} [MH]⁺: 1366.817; observed: 1366.909. The concentration of the peptide for NMR analysis was 9.7 mM.
peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG4_14) to give 15.4 mg of pure peptide (97.2% purity). Retention time on analytical RP-HPLC was 25.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{61}H_{109}N_{19}O_{17}[MH]^+: 1380.832; observed: 1380.929. The concentration of the peptide for NMR analysis was 13.2 mM.

**HPTULysGlu** (Ac-Arg Thr Val Lys Val Pro Gly Orn Glu Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 210.0 mg (0.053 mmol) of NovaSyn® TGR resin. The synthesis gave 304.3 mg of resin (>99% peptide). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG4_14) to give 18.6 mg of pure peptide (96.6% purity). Retention time on analytical RP-HPLC was 25.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{62}H_{111}N_{19}O_{17}[MH]^+: 1394.848; observed: 1394.983. The concentration of the peptide for NMR analysis was 13.2 mM.

**HPTUDapAad** (Ac-Arg Thr Val Dap Val Pro Gly Orn Aad Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 202.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 291.7 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG4_14) to give 4.1 mg of pure peptide (95.7% purity). Retention time on analytical RP-HPLC was 26.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{60}H_{107}N_{19}O_{17}[MH]^+: 1366.817; observed: 1366.897. The concentration of the peptide for NMR analysis was 6.0 mM.

**HPTUDabAad** (Ac-Arg Thr Val Dab Val Pro Gly Orn Aad Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 202.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 299.5 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG4_14) to give 7.8 mg of pure peptide (95.2% purity). Retention time on analytical RP-HPLC was 26.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{61}H_{109}N_{19}O_{17}[MH]^+: 1380.832; observed: 1380.958. The concentration of the peptide for NMR analysis was 11.0 mM.

**HPTUOrnAad** (Ac-Arg Thr Val Orn Val Pro Gly Orn Aad Ile Leu Gln-NH<sub>2</sub>)

The peptide was synthesized using 202.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 299.5 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0% yield). The peptide was purified by preparative RP-HPLC using a C4 column (PLG3_13) to give 6.7 mg of pure peptide (95.8% purity). Retention time on analytical RP-HPLC was 26.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{61}H_{109}N_{19}O_{17}[MH]^+: 1380.832; observed: 1380.958. The concentration of the peptide for NMR analysis was 11.0 mM.
mass spectrometry. Calculated for $\text{C}_{62}\text{H}_{111}\text{N}_{19}\text{O}_{17} [\text{MH}]^+ : 1394.848$; observed: 1395.985. The concentration of the peptide for NMR analysis was 9.6 mM.

**HPTULysAad** (Ac-Arg Thr Val Lys Val Pro Gly Orn Aad Ile Leu Gln-NH$_2$)

The peptide was synthesized using 202.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 299.5 mg of resin (>99% yield). The cleavage yielded 72.7 mg of crude peptide (85.0%). The peptide was purified by preparative RP-HPLC using a C4 (PLG4_14) to give 8.6 mg of pure peptide (96.7% purity). Retention time on analytical RP-HPLC was 26.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{63}\text{H}_{113}\text{N}_{19}\text{O}_{17} [\text{MH}]^+: 1408.863$; observed: 1408.902. The concentration of the peptide for NMR analysis was 12.2 mM.

**HPTFDapAsp** (Ac-Cys Arg Thr Dap Val Pro Gly Orn Asp Ile Leu Gln Cys-NH$_2$)

The peptide was synthesized using 204.9 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 351.1 mg of resin (>99% yield). The cleavage yielded 98.7 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 29.8 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{64}\text{H}_{115}\text{N}_{21}\text{O}_{19}\text{S}_2 [\text{MH}]^+: 1544.802$; observed: 1544.820. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC$_{18}$ cartridges (25% B) and a C18 column (PLG16_26) to give 1.6 mg of pure peptide (95.5% purity). Retention time on analytical RP-HPLC was 26.7 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{65}\text{H}_{115}\text{N}_{21}\text{O}_{19}\text{S}_2 [\text{MH}]^+: 1542.788$; observed: 1542.886. The concentration of the peptide for NMR analysis was 2.1 mM.

**HPTFDabAsp** (Ac-Cys Arg Thr Dab Val Pro Gly Orn Asp Ile Leu Gln Cys-NH$_2$)

The peptide was synthesized using 203.7 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 330.1 mg of resin (99.6% yield). The cleavage yielded 93.3 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 30.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{65}\text{H}_{115}\text{N}_{21}\text{O}_{19}\text{S}_2 [\text{MH}]^+: 1558.818$; observed: 1558.629. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC$_{18}$ cartridges (25% B) and a C18 column (PLG16_26) to give 2.2 mg of pure peptide (95.3% purity). Retention time on analytical RP-HPLC was 26.8 minutes. The identity of the peptide was confirmed by
MALDI-TOF mass spectrometry. Calculated for $\text{C}_{65}\text{H}_{113}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1556.804$; observed: 1556.703. The concentration of the peptide for NMR analysis was 2.8 mM.

**HPTFOrnAsp** (Ac-Cys Arg Thr Orn Val $^\text{D}$Pro Gly Orn Asp Ile Leu Gln Cys-NH$_2$)

The peptide was synthesized using 209.5 mg (0.052 mmol) of NovaSyn$^\text{®}$ TGR resin. The synthesis gave 325.5 mg of resin (84.4% yield). The cleavage yielded 88.1 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 30.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{66}\text{H}_{117}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1572.835$; observed: 1573.083. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 1 mg/mL (~1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 6 hours, the cyclized peptide was purified by preparative RP-HPLC using a C4 column (PLG8_18) to give 88.1 mg of pure peptide (95.9% purity). Retention time on analytical RP-HPLC was 27.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{66}\text{H}_{115}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1570.819$; observed: 1571.151. The concentration of the peptide for NMR analysis was 5.9 mM.

**HPTFLysAsp** (Ac-Cys Arg Thr Lys Val $^\text{D}$Pro Gly Orn Asp Ile Leu Gln Cys-NH$_2$)

The peptide was synthesized using 201.1 mg (0.050 mmol) of NovaSyn$^\text{®}$ TGR resin. The synthesis gave 329.9 mg of resin (99.8% yield). The cleavage yielded 94.6 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 30.6 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{67}\text{H}_{119}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1586.849$; observed: 1586.813. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak$^\text{®}$ plus short tC$_{18}$ cartridges (25% B) and a C18 column (PLG16_26) to give 2.8 mg of pure peptide (95.9% purity). Retention time on analytical RP-HPLC was 26.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{66}\text{H}_{117}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1584.835$; observed: 1584.713. The concentration of the peptide for NMR analysis was 3.5 mM.

**HPTFDapGlu** (Ac-Cys Arg Thr Dap Val $^\text{D}$Pro Gly Orn Glu Ile Leu Gln Cys-NH$_2$)

The peptide was synthesized using 204.2 mg (0.051 mmol) of NovaSyn$^\text{®}$ TGR resin. The synthesis gave 315.4 mg of resin (98.7% yield). The cleavage yielded 79.5 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 29.2 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for $\text{C}_{65}\text{H}_{115}\text{N}_{21}\text{O}_{19}\text{S}_2$ [MH]$: 1558.818$; observed: 1558.841. The peptide was dissolved in 1 mM...
pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC₁₈ cartridges (25% B) and a C₁₈ column (PLG16_26) to give 7.4 mg of pure peptide (96.6% purity). Retention time on analytical RP-HPLC was 25.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₅H₁₁₃N₂₁O₁₉S₂ [MH]+: 1556.804; observed: 1556.972. The concentration of the peptide for NMR analysis was 9.9 mM.

**HPTFDabGlu** (Ac-Cys Arg Thr Dab Val DPro Gly Orn Glu Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 204.2 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 313.7 mg of resin (98.6% yield). The cleavage yielded 74.7 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 29.4 minutes. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC₁₈ cartridges (25% B) and a C₁₈ column (PLG16_26) to give 4.0 mg of pure peptide (96.7% purity). Retention time on analytical RP-HPLC was 25.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₆H₁₁₅N₂₁O₁₉S₂ [MH]+: 1570.819; observed: 1571.019. The concentration of the peptide for NMR analysis was 5.3 mM.

**HPTFOrnGlu** (Ac-Cys Arg Thr Val Orn Val DPro Gly Orn Glu Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 205.1 mg (0.049 mmol) of NovaSyn® TGR resin. The synthesis gave 312.7 mg of resin (82.8% yield). The cleavage yielded 91.4 mg of crude peptide (>99.9% yield). Retention time on analytical RP-HPLC was 29.5 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₇H₁₁₉N₂₁O₁₉S₂ [MH]+: 1583.835; observed: 1585.075. The concentration of the peptide for NMR analysis was 6.4 mM.
HPTFLysGlu (Ac-Cys Arg Thr Lys Val D-Pro Gly Orn Glu Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 200.0 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 349.8 mg of resin (>99% yield). The cleavage yielded 76.2 mg of crude peptide (70.0% yield). Retention time on analytical RP-HPLC was 30.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₈H₁₂₁N₂₁O₁₉S₂ [MH]+: 1600.865; observed: 1600.896. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using a C₄ (PLG8_18) and a C18 column (PLG15_25) to give 2.0 mg of pure peptide (96.5% purity). Retention time on analytical RP-HPLC was 26.75 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₈H₁₁₉N₂₁O₁₉S₂ [MH]+: 1598.851; observed: 1599.250. The concentration of the peptide for NMR analysis was 2.5 mM.

HPTFDapAad (Ac-Cys Arg Thr Dap Val D-Pro Gly Orn Aad Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 203.8 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 333.1 mg of resin (99.8% yield). The cleavage yielded 84.6 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 29.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₆H₁₁₇N₂₁O₁₉S₂ [MH]+: 1572.834; observed: 1572.528. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC₁₈ cartridges (25% B) and a C18 column (PLG16_26) to give 7.3 mg of pure peptide (96.5% purity). Retention time on analytical RP-HPLC was 27.0 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₆H₁₁₅N₂₁O₁₉S₂ [MH]+: 1570.819; observed: 1570.923. The concentration of the peptide for NMR analysis was 9.3 mM.

HPTFDabAad (Ac-Cys Arg Thr Dap Val D-Pro Gly Orn Aad Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 201.8 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 322.4 mg of resin (99.3% yield). The cleavage yielded 80.7 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 29.8 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C₆₇H₁₁₉N₂₁O₁₉S₂ [MH]+: 1586.849; observed: 1586.415. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified...
by preparative RP-HPLC using Seppak® plus short tC_{18} cartridges (25% B) and C_{18} column and (PLG16_26) to give 6.6 mg of pure peptide (96.7% purity). Retention time on analytical RP-HPLC was 27.1 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{67}H_{117}N_{21}O_{19}S_{2} [MH]⁺: 1584.835; observed: 1585.058. The concentration of the peptide for NMR analysis was 8.3 mM.

HPTFOrnAad (Ac-Cys Arg Thr Orn Val^{D}Pro Gly Orn Aad Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 201.6 mg (0.050 mmol) of NovaSyn® TGR resin. The synthesis gave 307.7 mg of resin (80.0% yield). The cleavage yielded 69.1 mg of crude peptide (92.0% yield). Retention time on analytical RP-HPLC was 31.4 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{68}H_{121}N_{21}O_{19}S_{2} [MH]⁺: 1600.865; observed: 1601.087. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 1 mg/mL (~1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC_{18} cartridges (35% B) and a C_{4} column (PLG8_{18}) to give 3.1 mg of pure peptide (96.8% purity). Retention time on analytical RP-HPLC was 28.4 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{68}H_{119}N_{21}O_{19}S_{2} [MH]⁺: 1598.851; observed: 1599.270. The concentration of the peptide for NMR analysis was 3.5 mM.

HPTFLysAad (Ac-Cys Arg Thr Lys Val^{D}Pro Gly Orn Aad Ile Leu Gln Cys-NH₂)

The peptide was synthesized using 205.4 mg (0.051 mmol) of NovaSyn® TGR resin. The synthesis gave 333.4 mg of resin (99.5% yield). The cleavage yielded 101.6 mg of crude peptide (>99% yield). Retention time on analytical RP-HPLC was 30.5 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{69}H_{121}N_{21}O_{19}S_{2} [MH]⁺: 1614.881; observed: 1614.778. The peptide was dissolved in 1 mM pH 8 phosphate, citrate, and borate buffer at a concentration of 0.1 mg/mL (~0.1 mM). Granulated charcoal was added to the peptide solution, using up to 10:1 (w/w) ratio of charcoal to peptide [3]. After stirring over air for 4 hours, the cyclized peptide was purified by preparative RP-HPLC using Seppak® plus short tC_{18} cartridges (25% B) and a C_{18} column (PLG16_26) to give 2.7 mg of pure peptide (96.9% purity). Retention time on analytical RP-HPLC was 26.9 minutes. The identity of the peptide was confirmed by MALDI-TOF mass spectrometry. Calculated for C_{69}H_{119}N_{21}O_{19}S_{2} [MH]⁺: 1612.866; observed: 1612.696. The concentration of the peptide for NMR analysis was 2.0 mM.
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