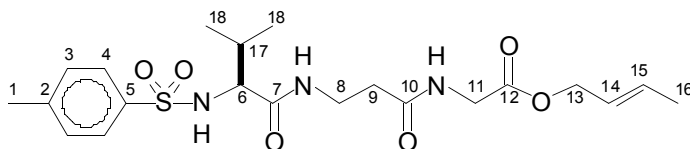


## Supplementary Material

### Analytical and Spectroscopic Data

6:

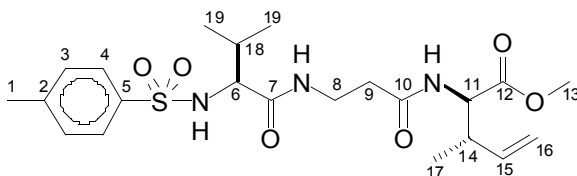


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.73 (d,  $J$  = 6.8 Hz, 3H, 18-H), 0.76 (d,  $J$  = 6.8 Hz, 3H, 18-H), 1.67 (dd,  $J$  = 6.5, 1.0 Hz, 3H, 16-H), 1.94 (m, 1H, 17-H), 2.32 (dt,  $J$  = 6.7, 4.9 Hz, 2H, 9-H), 2.40 (s, 3H, 1-H), 3.37 (dd,  $J$  = 5.9, 8.3 Hz, 1H, 6-H), 3.43 (m, 2H, 8-H), 3.84 (dd,  $J$  = 18.0, 5.5 Hz, 1H, 11-H), 4.03 (dd,  $J$  = 18.0, 6.0 Hz, 1H, 11-H), 4.54 (d,  $J$  = 6.7 Hz, 2H, 13-H), 5.54 (dtq,  $J$  = 15.2, 6.7, 1.6 Hz, 1H, 14-H), 5.62 (d,  $J$  = 8.5 Hz, 1H, TosN-H), 5.78 (dq,  $J$  = 15.2, 6.6 Hz, 1H, 15-H), 6.64 (t,  $J$  = 5.5 Hz, 1H, N-H), 7.18 (t,  $J$  = 6.0 Hz, 1H, N-H), 7.23 (d,  $J$  = 8.9 Hz, 2H, 3-H), 7.66 (d,  $J$  = 8.3 Hz, 2H, 4-H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 17.54 (q, C-18), 17.74 (q, C-16), 19.06 (q, C-18), 21.50 (q, C-1), 31.05 (d, C-17), 36.04, 36.13 (2t, C-8, C-9), 41.48 (t, C-11), 62.45 (d, C-6), 66.36 (t, C-13), 124.34 (d, C-14), 127.36 (2d, C-3), 129.55 (2d, C-4), 132.38 (d, C-15), 136.38 (s, C-2), 143.74 (s, C-5), 170.46, 171.06, 172.45 (3s, C-7, C-10, C-12).

C<sub>21</sub>H<sub>31</sub>N<sub>3</sub>O<sub>6</sub>S (453.56) calcd.: C 55.61 H 6.89 N 9.26 S 7.07; found: C 55.52 H 6.87 N 9.22 S 7.18.

7:

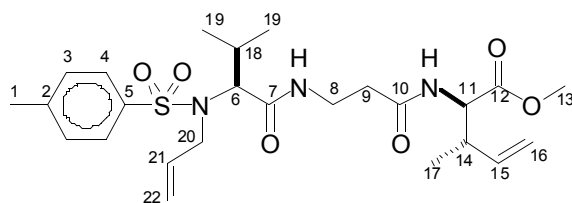


**<sup>1</sup>H NMR** (300 MHz, CD<sub>3</sub>OD):  $\delta$  = 0.81 (d,  $J$  = 6.4 Hz, 3H, 19-H), 0.86 (d,  $J$  = 6.5 Hz, 3H, 19-H), 1.03 (bs, 3H, 17-H), 1.84 (m, 1H, 18-H), 2.27 (m, 2H, 9-H), 2.40 (s, 3H, 1-H), 2.62 (m, 1H, 14-H), 3.15 (m, 2H, 8-H), 3.37 (bs, 1H, 6-H), 3.67 (s, 3H, 13-H), 4.42 (bs, 1H, 11-H), 5.03-5.09 (m, 2H, 16-H), 5.73 (m, 1H, 15-H), 7.33 (d,  $J$  = 8.4 Hz, 2H, 3-H), 7.69 (d,  $J$  = 7.6 Hz, 2H, 4-H).

**<sup>13</sup>C NMR** (75 MHz, CD<sub>3</sub>OD):  $\delta$  = 16.11 (q, C-17), 18.56, 19.56 (2q, C-19), 21.45 (q, C-1), 32.46 (d, C-18), 35.92, 36.69 (2t, C-8, C-9), 41.33 (d, C-14), 52.38 (q, C-13), 58.17 (d, C-11), 63.81 (d, C-6), 116.14 (t, C-16), 128.40 (2d, C-3), 130.53 (2d, C-4), 138.95 (s, C-2), 140.36 (d, C-15), 144.77 (s, C-5), 173.17, 173.52 (2s, C-7, C-10, C-12).

C<sub>22</sub>H<sub>33</sub>N<sub>3</sub>O<sub>6</sub>S (467.58) calcd.: C 56.51 H 7.11 N 8.99; found: C 56.24 H 7.08 N 8.72.

8:

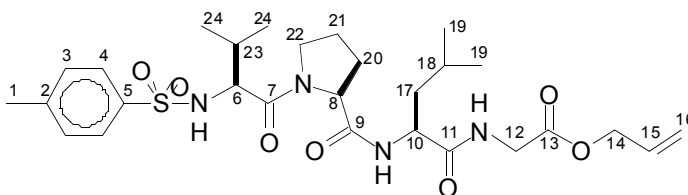


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.62 (d, *J* = 6.6 Hz, 3H, 19-H), 0.81 (d, *J* = 6.5 Hz, 3H, 19-H), 1.04 (d, *J* = 7.0 Hz, 3H, 17-H), 2.15 (m, 1H, 18-H), 2.34-2.47 (m, 2H, 9-H), 2.38 (s, 3H, 1-H), 2.65 (m, 1H, 14-H), 3.33 (m, 1H, 8-H), 3.45 (m, 1H, 8-H), 3.64 (d, *J* = 10.8 Hz, 1H, 6-H), 3.71 (s, 3H, 13-H), 3.86 (dd, *J* = 16.2, 6.0 Hz, 1H, 20-H), 4.13 (dd, *J* = 16.3, 7.0 Hz, 1H, 20-H), 4.60 (dd, *J* = 8.6, 5.2 Hz, 1H, 11-H), 5.01-5.18 (m, 4H, 16-H, 22-H), 5.62-5.84 (m, 2H, 15-H, 21-H), 6.03 (d, *J* = 8.2 Hz, 1H, N-H), 6.63 (bs, 1H, N-H), 7.23 (d, *J* = 8.1 Hz, 2H, 3-H), 7.67 (d, *J* = 8.2 Hz, 2H, 4-H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ = 15.54 (q, C-17), 19.03, 19.45 (2q, C-19), 21.26 (q, C-1), 27.00 (d, C-18), 35.12, 35.26 (2t, C-8, C-9), 40.26 (d, C-14), 47.08 (t, C-20), 51.92 (q, C-13), 55.79 (d, C-11), 66.04 (d, C-6), 116.23 (t, C-16), 117.31 (d, C-22), 127.23 (2d, C-3), 129.25 (2d, C-4), 134.86 (d, C-21), 137.43 (s, C-2), 138.21 (d, C-15), 143.16 (s, C-5), 169.49, 170.72, 171.51 (3s, C-7, C-10, C-12).

C<sub>25</sub>H<sub>37</sub>N<sub>3</sub>O<sub>6</sub>S (507.65) calcd.: C 59.15 H 7.35 N 8.28 S 6.32; found: C 59.11 H 7.44 N 8.13 S 6.54.

9:

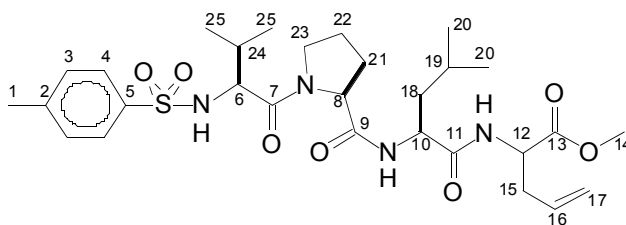


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.82 (d, *J* = 6.1 Hz, 3H, 19-H), 0.84 (d, *J* = 6.0 Hz, 3H, 19-H), 0.86 (d, *J* = 6.6 Hz, 3H, 24-H), 0.91 (d, *J* = 6.8 Hz, 3H, 24-H), 1.47-2.14 (m, 8H, 17-H, 18-H, 20-H, 21-H, 23-H), 2.39 (s, 3H, 1-H), 3.13 (m, 1H, 22-H), 3.38 (m, 1H, 22-H), 3.60 (dd, *J* = 9.9, 6.5 Hz, 1H, 6-H), 3.94 (dd, *J* = 18.2, Hz, 1H, 12-H), 4.02 (dd, *J* = 18.2, 5.3 Hz, 1H, 12-H), 4.13 (dd, *J* = 8.4, 2.6 Hz, 1H, 8-H), 4.33 (m, 1H, 10-H), 4.58 (dt, *J* = 6.2, 1.3 Hz, 2H, 14-H), 5.22 (dt, *J* = 10.4, 1.3 Hz, 1H, 16-H), 5.28 (dt, *J* = 17.2, 1.4 Hz, 1H, 16-H), 5.86 (ddt, *J* = 17.1, 10.4, 6.3 Hz, 1H, 15-H), 6.39 (d, *J* = 9.9 Hz, 1H, TosN-H), 6.76 (t, *J* = 5.4 Hz, 1H, GlyN-H), 7.17 (d, *J* = 7.8 Hz, 1H, LeuN-H), 7.26 (d, *J* = 8.1 Hz, 2H, 3-H), 7.69 (d, *J* = 8.3 Hz, 2H, 4-H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ = 17.68, 19.07 (2q, C-24), 21.47 (q, C-1), 21.77, 22.88 (2q, C-19), 24.57 (d, C-18), 24.90 (t, C-21), 27.14 (t, C-20), 31.68 (d, C-23), 40.60 (t, C-17), 41.18 (t, C-12), 47.24 (t, C-22), 51.90 (d, C-10), 59.34 (d C-8), 59.67 (d, C-6); 65.87 (t, C-14), 118.82 (t, C-16), 127.41 (2d, C-3), 129.43 (2d, C-4), 131.48 (d, C-15), 136.01 (s, C-2), 143.59 (s, C-5), 169.31, 170.92, 171.14, 172.06 (4s, C-7, C-9, C-11, C-13).

C<sub>28</sub>H<sub>42</sub>N<sub>4</sub>O<sub>7</sub>S (578.73) calcd.: C 58.11 H 7.32 N 9.68 S 5.54; found: C 57.94 H 7.29 N 9.53 S 5.68.

10:

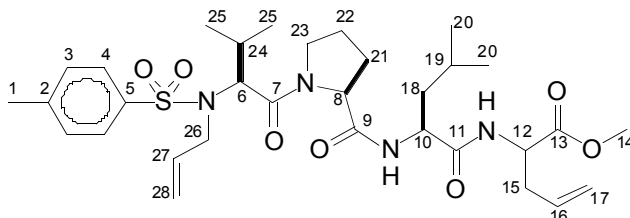


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.82 (d, *J* = 6.1 Hz, 3H, 20-H), 0.86 (d, *J* = 6.2 Hz, 3H, 20-H), 0.89 (d, *J* = 6.8 Hz, 3H, 25-H), 0.94 (d, *J* = 6.7 Hz, 3H, 25-H), 1.46-2.09 (m, 8H, 18-H, 19-H, 21-H, 22-H, 24-H), 2.39 (s, 3H, 1-H), 2.47 (m, 2H, 15-H), 3.12 (m, 1H, 23-H), 3.37 (m, 1H, 23-H), 3.64 (dd, *J* = 10.1, 6.3 Hz, 1H, 6-H), 3.69 (s, 3H, 14-H), 4.04 (dd, *J* = 8.4, 2.7 Hz, 1H, 8-H), 4.30 (m, 1H, 12-H), 4.56 (m, 1H, 10-H), 5.04 (d, *J* = 15.4 Hz, 1H, 17-H), 5.05 (d, *J* = 11.6 Hz, 1H, 17-H), 5.65 (m, 1H, 16-H), 6.06 (d, *J* = 10.0 Hz, 1H, TosN-H), 6.59 (d, *J* = 7.7 Hz, 1H, N-H), 7.00 (d, *J* = 7.7 Hz, 1H, N-H), 7.27 (d, *J* = 8.2 Hz, 2H, 3-H), 7.69 (d, *J* = 8.3 Hz, 2H, 4-H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 17.28, 18.99 (2q, C-25), 21.27 (q, C-1), 21.66, 22.66 (2q, C-20), 24.42 (d, C-19), 25.12 (t, C-22), 26.85 (t, C-21), 31.40 (d, C-24), 36.04 (t, C-15), 40.57 (t, C-18), 46.99 (t, C-23), 51.44 (q, C-14), 51.66 (d, C-12), 52.07 (d, C-10), 59.13 (d, C-8), 59.47 (d, C-6), 118.79 (t, C-17), 127.25 (2d, C-3), 129.18 (2d, C-4), 132.03 (d, C-16), 136.61 (s, C-2), 143.36 (s, C-5), 170.47, 170.85, 171.17, 171.60 (4s, C-7, C-9, C-11, C-13).

**HMRS** calcd for  $\text{C}_{29}\text{H}_{45}\text{N}_4\text{O}_7\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 593.2993, found: 593.3022;  
calcd for  $\text{C}_{29}\text{H}_{44}\text{N}_4\text{O}_7\text{SNa}$  ( $[\text{M}+\text{Na}]^+$ ): 615.2812, found: 615.2847.

11:

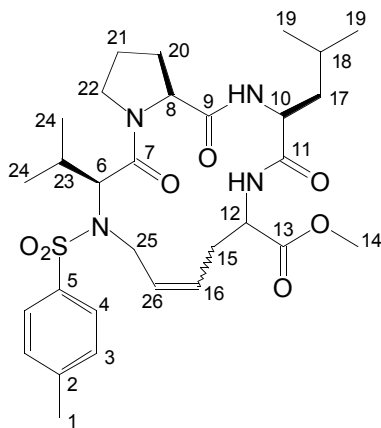


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.83 (d,  $J$  = 6.1 Hz, 3H, 20-H), 0.85 (d,  $J$  = 7.2 Hz, 3H, 20-H), 0.88 (d,  $J$  = 6.7 Hz, 3H, 25-H), 0.89 (d,  $J$  = 6.6 Hz, 3H, 25-H), 1.39-1.49 (m, 1H, 19-H), 1.53-1.89 (m, 2H, 18-H), 1.89 (m, 1H, 24-H), 1.98-2.20 (m, 4H, 21-H, 22-H), 2.38 (s, 3H, 1-H), 2.49 (m, 2H, 15-H), 3.52 (m, 1H, 23-H), 3.65-3.76 (m, 1H, 23-H), 3.69 (s, 3H, 14-H), 3.96 (dd,  $J$  = 16.6, 5.3 Hz, 1H, 26-H), 4.22-4.32 (m, 3H, 6-H, 8-H, 10-H), 4.39 (dd,  $J$  = 16.5, 7.7 Hz, 1H, 26-H), 4.56 (m, 1H, 12-H), 4.99-5.15 (m, 4H, 17-H, 28-H), 5.63 (m, 1H, 16-H), 5.87 (m, 1H, 27-H), 6.70 (d,  $J$  = 7.7 Hz, 1H, N-H), 6.86 (d,  $J$  = 7.9 Hz, 1H, N-H), 7.23 (d,  $J$  = 7.9 Hz, 2H, 3-H), 7.58 (d,  $J$  = 8.3 Hz, 2H, 4-H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 18.59, 19.75 (2q, C-25), 21.25 (s, C-1), 21.78, 22.57 (2q, C-20), 24.50 (d, C-19), 24.66 (t, C-22), 27.32 (t, C-21), 28.93 (d, C-24), 36.06 (t, C-15), 40.49 (t, C-18), 47.31 (t, C-23), 51.43 (q, C-14), 51.70 (d, C-12), 51.91 (t, C-26), 52.07 (d, C-10), 59.89 (d, C-8), 62.16 (d, C-6), 116.64 (t, C-28), 118.78 (t, C-17), 127.04 (2d, C-3), 129.18 (2d, C-4), 132.05 (d, C-16), 135.71 (d, C-27), 137.09 (s, C-2), 143.30 (s, C-5), 170.73, 170.84, 171.19, 171.61 (4s, C-7, C-9, C-11, C-13).

**HMRS** calcd for  $\text{C}_{32}\text{H}_{49}\text{N}_4\text{O}_7\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 633.3305, found: 633.3329;  
calcd for  $\text{C}_{32}\text{H}_{48}\text{N}_4\text{O}_7\text{SNa}$  ( $[\text{M}+\text{Na}]^+$ ): 655.3124, found: 655.3154.

12:



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.53 (d,  $J$  = 6.1 Hz, 3H, 19-H), 0.83 (d,  $J$  = 6.4 Hz, 3H, 19-H), 0.89 (d,  $J$  = 6.6 Hz, 3H, 24-H), 0.94 (d,  $J$  = 6.6 Hz, 3H, 24-H), 1.48-2.33 (m, 8H, 17-H, 18-H, 20-H, 21-H, 23-H), 2.40 (s, 3H, 1-H), 2.82 (m, 2H, 15-H), 3.67 (s, 3H, 14-H), 3.64-3.70 (m, 3H, 22-H, 25-H), 3.82 (dd,  $J$  = 16.5, 10.5 Hz,

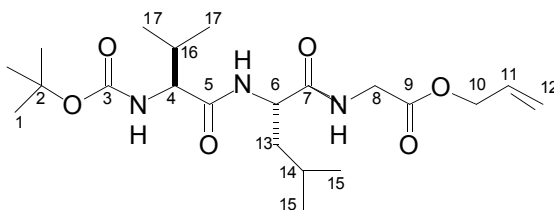
1H, 25-H), 3.96 (m, 1H, 10-H), 4.09 (m, 1H, 8-H), 4.23 (d,  $J = 10.5$  Hz, 1H, 6-H), 4.74 (m, 1H, 12-H), 5.19 (t,  $J = 10.5$  Hz, 1H, 16-H), 5.47 (d,  $J = 8.4$  Hz, 1H, Leu-NH), 5.55 (t,  $J = 10.9$  Hz, 1H, 26-H), 7.27 (d,  $J = 8.3$  Hz, 2H, 3-H), 7.70 (d,  $J = 8.3$  Hz, 2H, 4-H), 8.61 (d,  $J = 8.3$  Hz, 1H, NH).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 19.11$  (2q, C-24), 20.73 (q, C-19), 21.50 (q, C-1), 23.17 (q, C-19), 24.34 (d, C-18), 25.72 (t, C-21), 27.68 (d, C-23), 28.36, 28.63 (2t, C-15, C-20), 40.66, 40.81 (2t, C-17, C-25), 47.25 (t, C-22), 52.36, 52.41 (d, C-12; q, C-14), 54.79 (d, C-10), 56.94 (d, C-8), 61.52 (d, C-6), 127.80 (d, C-3), 128.56, 128.62 (2d, C-16, C-26), 129.52 (d, C-4), 136.97 (s, C-2), 143.73 (s, C-5), 167.61, 171.35, 171.99, 172.71 (4s, C-7, C-), C-11, C-13).

HMRS calcd for  $\text{C}_{30}\text{H}_{45}\text{N}_4\text{O}_7\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 605.2993, found: 605.3029;

calcd for  $\text{C}_{30}\text{H}_{44}\text{N}_4\text{O}_7\text{SNa}$  ( $[\text{M}+\text{Na}]^+$ ): 627.2812, found: 627.2820.

13:

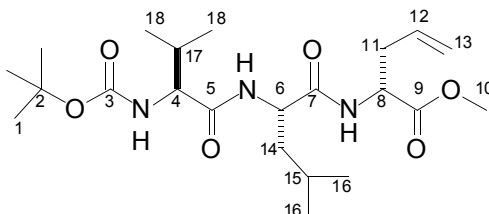


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.86$ -0.94 (m, 12H, 15-H, 17-H), 1.40 (s, 9H, 1-H), 1.51-1.70 (m, 3H, 13-H, 14-H), 2.10 (m, 1H, 16-H), 3.88 (m, 1H, 6-H), 3.99 (m, 2H, 8-H), 4.59 (d,  $J = 5.8$  Hz, 2H, 10-H), 5.15 (bs, 1H, BocN-H), 5.22 (dd,  $J = 10.4, 1.2$  Hz, 1H, 12-H), 5.29 (dd,  $J = 17.2, 1.3$  Hz, 1H, 12-H), 5.85 (ddt,  $J = 17.1, 10.6, 5.9$  Hz, 1H, 11-H), 6.65 (bs, 1H, N-H), 7.03 (bs, 1H, N-H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.65, 19.08$  (2q, C-17), 21.59, 22.71 (2q, C-15), 24.43 (d, C-14), 28.05 (3q, C-1), 30.29 (d, C-16), 40.53 (t, C-8), 41.00 (t, C-13), 51.27 (d, C-6), 60.13 (d, C-4), 65.69 (t, C-10), 79.97 (s, C-2), 118.65 (t, C-12), 131.29 (d, C-11), 155.90 (s, C-3), 168.97, 171.69, 172.07 (3s, C-5, C-7, C-9).

$\text{C}_{21}\text{H}_{37}\text{N}_3\text{O}_6$  (427.54) calcd.: C 59.00 H 8.72 N 9.83; found: C 59.15 H 8.86 N 9.80.

14:

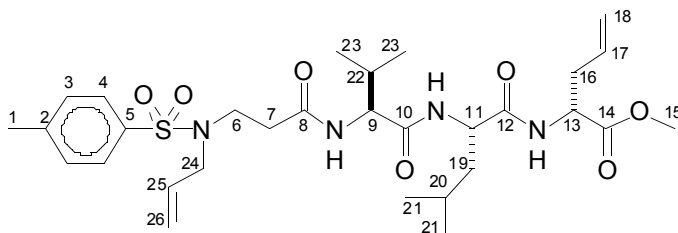


$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.87$ -0.94 (m, 12H, 16-H, 18-H), 1.41 (s, 9H, 1-H), 1.48-1.66 (m, 3H, 15-H, 14-H), 2.10 (m, 1H, 17-H), 2.49 (m, 2H, 11-H), 3.70 (s, 3H, 10-H), 3.88 (m, 1H, 4-H), 4.45 (m, 1H, 8-H), 4.57 (m, 1H, 6-H), 5.06-5.09 (m, 1H, BocN-H), 5.07 (d,  $J = 9.6$  Hz, 1H, 13-H), 5.08 (d,  $J = 16.9$  Hz, 1H, 13-H), 5.62 (ddt,  $J = 17.2, 9.6, 7.0$  Hz, 1H, 12-H), 6.51 (d,  $J = 7.7$  Hz, 1H, N-H), 6.72 (d,  $J = 7.7$  Hz, 1H, N-H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.58, 19.06$  (2q, C-18), 21.77, 22.60 (2q, C-16), 24.38 (d, C-15), 28.05 (3q, C-1), 30.40 (d, C-17), 36.05 (t, C-11), 40.77 (t, C-14), 51.32 (d, C-6), 51.52 (q, C-10), 52.08 (d, C-8), 59.82 (d, C-4), 79.77 (s, C-2), 119.01 (t, C-13), 131.76 (d, C-12), 155.65 (s, C-3), 171.15, 171.48, 171.52 (3s, C-5, C-7, C-9).

$\text{C}_{22}\text{H}_{39}\text{N}_3\text{O}_6$  (441.56) calcd.: C 59.84 H 8.90 N 9.52; found: C 59.63 H 8.89 N 9.38

15:



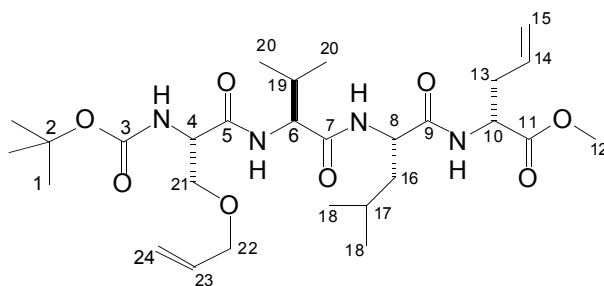
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.82-0.91 (m, 12H, 21-H, 23-H), 1.46-1.66 (m, 3H, 19-H, 20-H), 1.99 (m, 1H, 22-H), 2.37 (s, 3H, 1-H), 2.40-2.57 (m, 3H, 7-H, 16-H), 2.65-2.73 (m, 1H, 16-H), 3.38 (m, 2H, 6-H), 3.66 (s, 3H, 15-H), 3.74 (d, *J* = 5.1 Hz, 2H, 24-H), 4.40 (m, 1H, 11-H), 4.59-4.68 (m, 2H, 9-H, 13-H), 4.96-5.16 (m, 4H, 18-H, 26-H), 5.48-5.69 (m, 2H, 17-H, 25-H), 7.20-7.31 (m, 2H, je N-H), 7.25 (d, *J* = 8.0 Hz, 2H, 3-H), 7.65 (d, *J* = 8.3 Hz, 2H, 4-H), 7.66 (d, *J* = 8.2 Hz, 1H, N-H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ = 18.45, 19.09 (2q, C-23), 21.43 (q, C-1), 22.41, 22.51 (2q, C-21), 24.62 (d, C-20), 31.19 (d, C-22), 36.31 (t, C-7), 38.55 (t, C-16), 41.15 (t, C-19), 43.99 (t, C-6), 51.62 (q, C-15), 51.72 (t, C-24), 51.82 (d, C-13), 52.20 (d, C-11), 58.45 (d, C-9), 118.71, 119.08 (2t, C-18, C-26), 127.23 (d, C-3), 129.67 (d, C-4), 132.34, 132.85 (2d, C-17, C-25), 136.38 (s, C-2), 143.35 (s, C-5), 170.65, 171.25, 171.89, 171.97 (4s, C-8, C-10, C-12, C-14).

**HMRS** calcd for C<sub>30</sub>H<sub>47</sub>N<sub>4</sub>O<sub>7</sub>S ([M+H]<sup>+</sup>): 607.3149, found: 607.3221;

calcd for C<sub>30</sub>H<sub>46</sub>N<sub>4</sub>O<sub>7</sub>SNa ([M+Na]<sup>+</sup>): 629.2968, found: 629.3007.

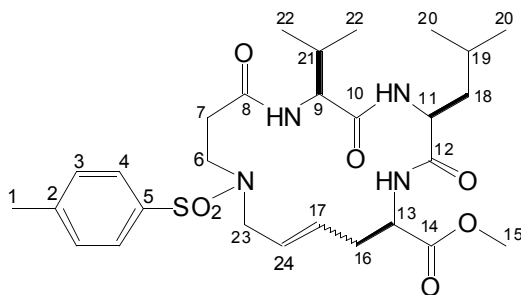
16:



**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ = 0.82-0.94 (m, 12H, 18-H, 20-H), 1.40 (s, 9H, 1-H), 1.48- 1.69 (m, 3H, 16-H, 17-H), 2.11 (m, 1H, 19-H), 2.47 (m, 1H, 13-H), 2.52 (m, 1H, 13-H), 3.55 (m, 1H, 21-H), 3.68 (s, 3H, 12-H), 3.74 (m, 1H, 21-H), 3.94-3.98 (m, 2H, 22-H), 4.23 (m, 1H, 4-H), 4.29 (m, 1H, 6-H), 4.51 (m, 1H, 8-H), 4.58 (m, 1H, 10-H), 5.03 (d, *J* = 12.0 Hz, 1H, 15-H), 5.06 (d, *J* = 17.1 Hz, 1H, 15-H), 5.14 (d, *J* = 10.3 Hz, 1H, 24-H), 5.21 (d, *J* = 17.4 Hz, 1H, 24-H), 5.50 (bs, 1H, BocNH), 5.65 (m, 1H, 14-H), 5.80 (m, 1H, 23-H), 6.80-7.10 (m, 3H, NH).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>): δ = 17.18 (q, C-20), 19.11 (q, C-20), 21.39 (q, C-18), 22.72 (q, C-18), 24.47 (d, C-17), 28.00 (q, C-1), 28.04 (d, C-19), 35.96 (t, C-13), 40.32 (t, C-16), 51.31, 51.61, 51.79, 52.00 (4d, C-4, C-8, C-10, C-12), 58.76 (d, C-6), 69.03 (t, C-21), 72.08 (t, C-22), 80.53 (s, C-2), 117.69 (t, C-24), 118.47 (t, C-15), 132.30 (d, C-14), 133.55 (d, C-23), 155.87 (s, C-3), 170.48, 171.27, 171.41, 171.54 (4s, C-5, C-7, C-9, C-11).  
C<sub>28</sub>H<sub>48</sub>N<sub>4</sub>O<sub>8</sub> (568.70) calcd.: C 59.14 H 8.51 N 9.85; found: C 59.91 H 8.42 N 9.80.

17:

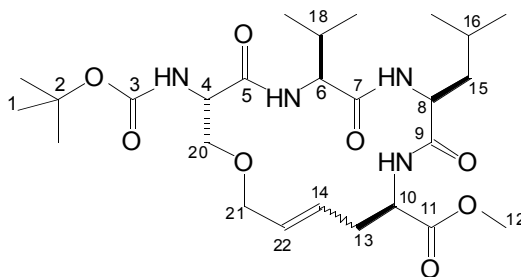


**<sup>1</sup>H NMR** (500 MHz, d<sub>7</sub>-DMF): δ = 0.86 (d, *J* = 6.3 Hz, 3H, 20-H), 0.88 (d, *J* = 6.4 Hz, 3H, 20-H), 0.99 (d, *J* = 7.0 Hz, 3H, 22-H), 1.00 (d, *J* = 7.0 Hz, 3H, 22-H), 1.62-1.70 (m, 2H, 18-H, 19-H), 1.76 (m, 1H, 18-H), 2.11 (m, 1H, 21-H), 2.43 (s, 3H, 1-H), 2.44-2.52 (m, 3H, 6-H, 16-H), 2.69 (m, 1H, 6-H), 3.26 (m, 1H, 7-H), 3.51 (m, 1H, 7-H), 3.64 (s, 3H, 15-H), 3.75 (dd, *J* = 14.7, 6.3 Hz, 1H, 23-H), 3.81 (dd, *J* = 14.8, 7.1 Hz, 1H, 23-H), 3.97 (dd, *J* = 6.0, 5.7 Hz, 1H, 9-H), 4.43 (m, 1H, 11-H), 4.59 (m, 1H, 13-H), 5.43 (dt, *J* = 15.4, 6.7 Hz, 1H, 24-H), 5.64 (dt, *J* = 15.4, 7.0 Hz, 1H, 17-H), 7.47 (d, *J* = 8.0 Hz, 2H, 3-H), 7.62 (d, *J* = 8.0 Hz, 1H, NH), 7.71 (d, *J* = 8.3 Hz, 1H, LeuNH), 7.75 (d, *J* = 8.0 Hz, 2H, 4-H), 8.15 (d, *J* = 6.1 Hz, 1H, ValNH).

**<sup>13</sup>C NMR** (125 MHz, d<sub>7</sub>-DMF): δ = 18.67, 19.50 (2q, C-22), 21.23 (q, C-1), 21.35, 23.38 (2q, C-20), 25.13 (d, C-19), 30.43 (d, C-21), 33.88 (t, C-16), 40.62 (t, C-18), 43.28 (t, C-6), 50.18 (t, C-23), 51.94, 52.27, 52.39 (d, C-11; d, C-13; q, C-15), 61.86 (d, C-9), 127.81 (d, C-3), 128.84 (d, C-24), 130.42 (d, C-4), 131.29 (d, C-17), 137.32 (s, C-2), 144.18 (s, C-5), 171.89, 171.98, 172.50, 172.76 (4s, C-8, C-10, C-12, C-14). (C-7 together with solvent).

C<sub>28</sub>H<sub>42</sub>N<sub>4</sub>O<sub>7</sub>S (578.73) calcd.: C 58.11 H 7.32 N 9.68; found: C 58.15 H 7.38 N 9.27.

18:



**<sup>1</sup>H NMR** (300 MHz, CD<sub>3</sub>OD): δ = 0.92 (d, *J* = 6.2 Hz, 3H, 17-H), 0.94 (d, *J* = 6.9 Hz, 3H, 17-H), 0.96 (d, *J* = 6.0 Hz, 3H, 19-H), 0.97 (d, *J* = 6.2 Hz, 3H, 19-H), 1.42 (s, 9H, 1-H), 1.63 (m, 2H, 15-H), 1.69 (m, 1H, 16-H), 2.10 (m, 1H, 18-H), 2.35 (m, 1H, 13-H), 2.60 (m, 1H, 13-H), 1.57 (m, 2H, 20-H), 3.71 (s, 3H, 12-H), 3.84 (d, *J* = 11.8 Hz, 1H, 21-H), 3.93 (d, *J* = 11.5 Hz, 1H, 21-H), 4.26 (m, 1H, 4-H), 4.28 (d, *J* = 6.9 Hz, 1H, 6-H), 4.37 (m, 1H, 8-H), 4.66 (dd, *J* = 9.8, 3.3 Hz, 1H, 10-H), 5.58 (m, 2H, 14-H, 22-H).

**<sup>13</sup>C NMR** (75 MHz, CD<sub>3</sub>OD): δ = 18.44, 19.75 (2q, C-17), 22.56, 22.97 (2q, C-19), 25.99 (d, C-16), 28.65 (q, C-1), 32.29 (d, C-18), 34.88 (t, C-13), 41.74 (t, C-15), 52.80, 52.85 (d, C-10; q, C-12), 53.70 (d, C-8), 55.40 (d, C-4), 62.07 (d, C-6), 70.77 (t, C-20), 72.19 (t, C-21), 80.76 (s, C-2), 128.18, 130.34 (2d, C-14, C-22), 157.42 (s, C-3), 172.79, 173.04, 173.29, 173.69 (4s, C-5, C-7, C-9, C-11).

**HMRS** calcd for C<sub>26</sub>H<sub>45</sub>N<sub>4</sub>O<sub>8</sub> ([M+H]<sup>+</sup>): 541.3222, found: 541.3256;

calcd for C<sub>26</sub>H<sub>44</sub>N<sub>4</sub>O<sub>8</sub>Na ([M+Na]<sup>+</sup>): 563.3041, found: 563.3052.