Supplementary Material



HPLC and MS spectra of compounds

Supplementary Figure 1. A) The structure Ascaphin-8; B) The HPLC of purified Ascaphin-8; C) MS spectrum of Ascaphin-8 calculated for $C_{97}H_{164}N_{24}O_{22}$ 2017.25; found $[M+2H]^{2+}$: 1009.91; $[M+3H]^{3+}$: 673.76; $[M+4H]^{4+}$: 505.56.



Supplementary Figure 2. A) The structure A8-1-*o*; B) The HPLC of purified A8-1-*o*; C) MS spectrum of A8-1-*o* calculated for $C_{105}H_{172}N_{24}O_{20}S_2$ 2153.26; found $[M+2H]^{2+}$: 1078.8; $[M+3H]^{3+}$: 719.35; $[M+4H]^{4+}$: 539.9.



Supplementary Figure 3. A) The structure A8-1-*m*; B) The HPLC of purified A8-1-*m*; C) MS spectrum of A8-1-*m* calculated for $C_{105}H_{172}N_{24}O_{20}S_2$ 2153.26; found $[M+2H]^{2+}$: 1078.35; $[M+3H]^{3+}$: 719.4; $[M+4H]^{4+}$: 539.9.



Supplementary Figure 4. A) The structure A8-1-*p*; B) The HPLC of purified A8-1-*p*; C) MS spectrum of A8-1-*p* calculated for $C_{105}H_{172}N_{24}O_{20}S_2$ 2153.26; found $[M+2H]^{2+}$: 1078.5; $[M+3H]^{3+}$: 719.45; $[M+4H]^{4+}$: 540.1.



Supplementary Figure 5. A) The structure A8-2-*o*; B) The HPLC of purified A8-2-*o*; C) MS spectrum of A8-2-*o* calculated for $C_{106}H_{172}N_{24}O_{22}S_2$ 2197.24; found $[M+2H]^{2+}$: 1100.31; $[M+3H]^{3+}$: 734.01; $[M+4H]^{4+}$: 550.86.



Supplementary Figure 6. A) The structure A8-2-*m*; B) The HPLC of purified A8-2-*m*; C) MS spectrum of A8-2-*m* calculated for $C_{106}H_{172}N_{24}O_{22}S_2 2197.24$; found $[M+2H]^{2+}$: 1100.46; $[M+3H]^{3+}$: 734.01; $[M+4H]^{4+}$: 550.66.



Supplementary Figure 7. A) The structure A8-2-*p*; B) The HPLC of purified A8-2-*p*; C) MS spectrum of A8-2-*p* calculated for $C_{106}H_{172}N_{24}O_{22}S_2$ 2197.24; found $[M+2H]^{2+}$: 1100.4; $[M+3H]^{3+}$: 733.9; $[M+4H]^{4+}$: 550.9.



Supplementary Figure 8. A) The structure A8-3-*o*; B) The HPLC of purified A8-3-*o*; C) MS spectrum of A8-3-*o* calculated for $C_{104}H_{167}N_{23}O_{22}S_2$ 2154.2; found $[M+2H]^{2+}$: 1079; $[M+3H]^{3+}$: 719.6; $[M+4H]^{4+}$: 539.85.



Supplementary Figure 9. A) The structure A8-3-*m*; B) The HPLC of purified A8-3-*m*; C) MS spectrum of A8-3-*m* calculated for $C_{104}H_{167}N_{23}O_{22}S_2$ 2154.2; found [M+2H]²⁺: 1078.75; [M+3H]³⁺: 719.55; [M+4H]⁴⁺: 540.



Supplementary Figure 10. A) The structure A8-3-*p*; B) The HPLC of purified A8-3-*p*; C) MS spectrum of A8-3-*p* calculated for $C_{104}H_{167}N_{23}O_{22}S_2$ 2154.2; found $[M+2H]^{2+}$: 1078.4; $[M+3H]^{3+}$: 719.5; $[M+4H]^{4+}$: 539.8.



Supplementary Figure 11. A) The structure A8-4-*Dp*; B) The HPLC of purified A8-4-*Dp*; C) MS spectrum of A8-4-*Dp* calculated for $C_{110}H_{17}1N_{23}O_{22}S_2$ 2230.24; found $[M+2H]^{2+}$: 1116.25; $[M+3H]^{3+}$: 744.8; $[M+4H]^{4+}$: 558.8.