Supporting Information

Reaction of chloroacetyl-modified peptides with mercaptoundecahydrododecaborate (BSH) is accelerated by basic amino acid residues in the peptide

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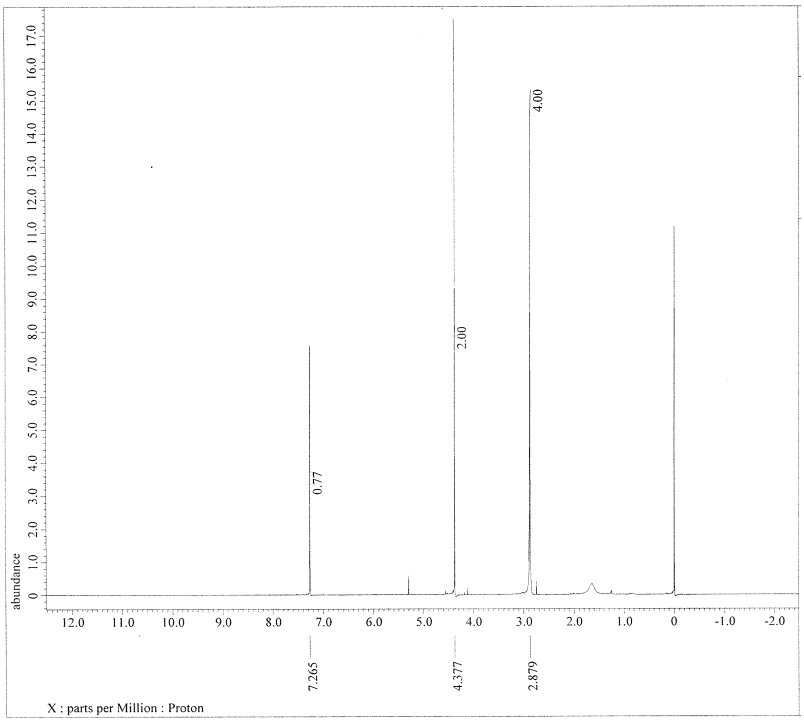

Figure S1. ^{1}H NMR spectrum of ClAc-OSu in $CDCl_3$ at room temperature. 400 MHz: δ = 4.38 (2H, s, ClC*H*$_2$), 2.88 (4H, s, C*H*$_2$C*H*$_2$).

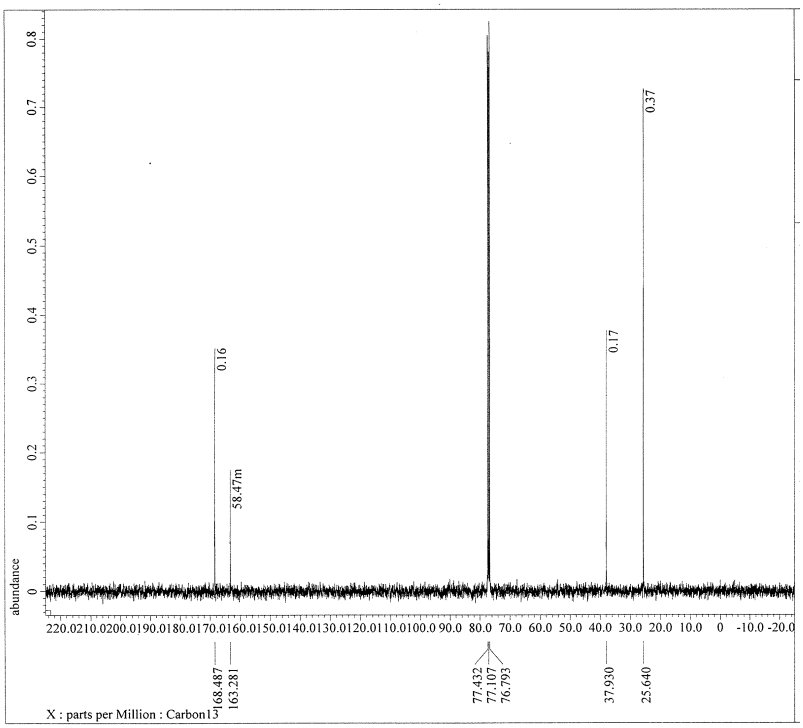

Figure S2. ^{13}C NMR spectrum of ClAc-OSu in $CDCl_3$ at room temperature. 400 MHz: δ = 25.6 (*C*H$_2$*C*H$_2$), 37.9 (*C*H$_2$Cl), 163.3 (O*C*=O), 168.5 (N*C*=O).

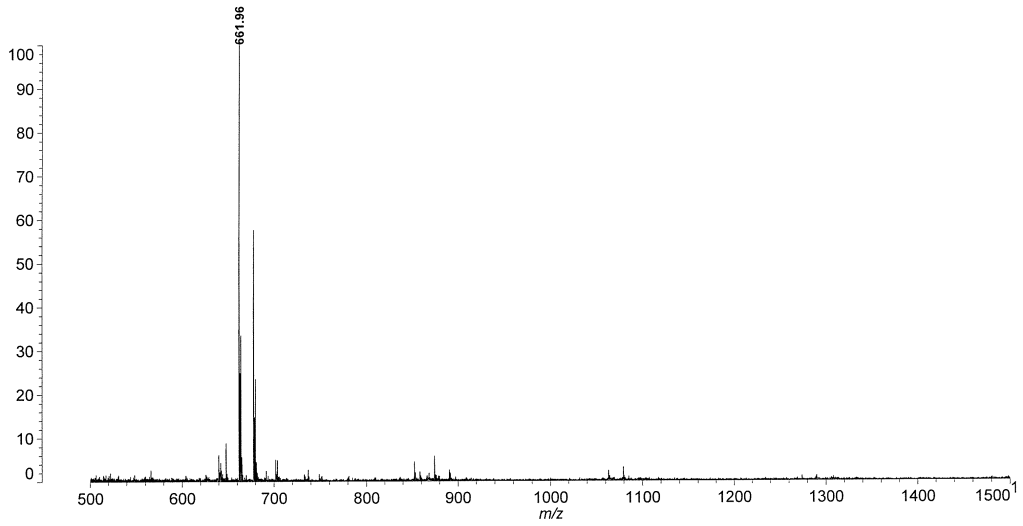

Figure S3. MALDI-TOF mass spectrum of **Cl-3A**. α-CHCA was used as a matrix. **Cl-3A**: calcd. $[M+Na]^+$ = 664.28 and obsd. $[M+Na]^+$ = 661.96.

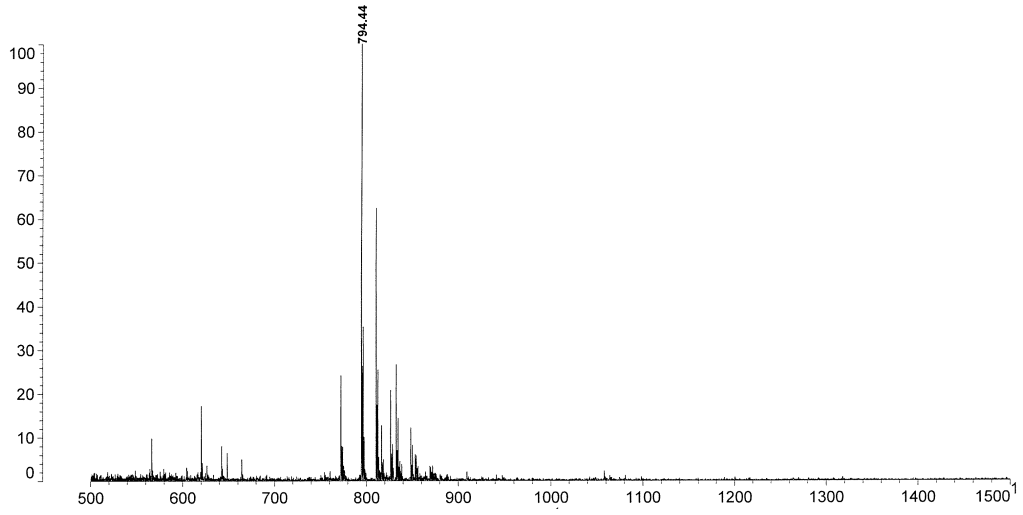

Figure S4. MALDI-TOF mass spectrum of **Cl-3D**. α-CHCA was used as a matrix. **Cl-3D**: calcd. $[M+Na]^+$ = 796.26 and obsd. $[M+Na]^+$ = 794.44.

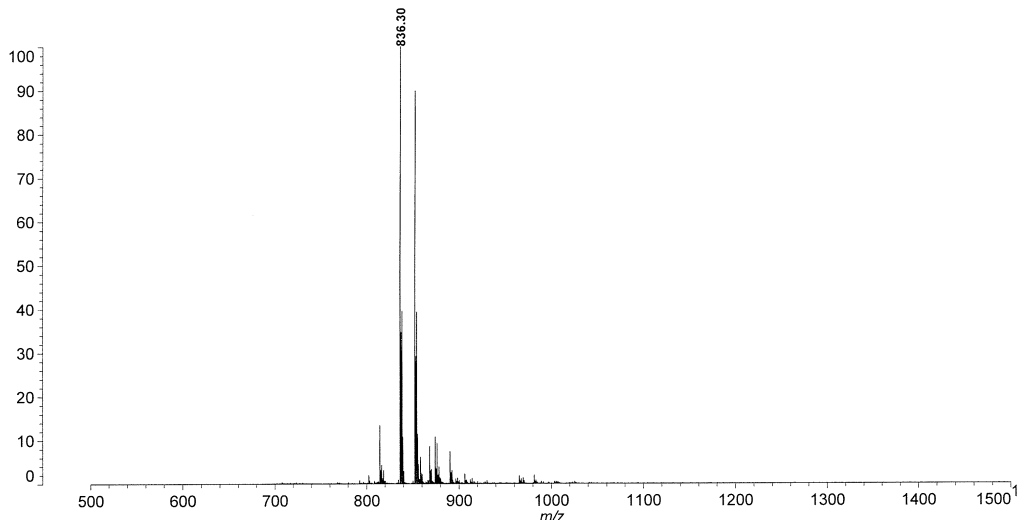

Figure S5. MALDI-TOF mass spectrum of **Cl-3E**. α-CHCA was used as a matrix. **Cl-3E**: calcd. $[M+H]^+$ = 838.30 and obsd. $[M+H]^+$ = 836.30.

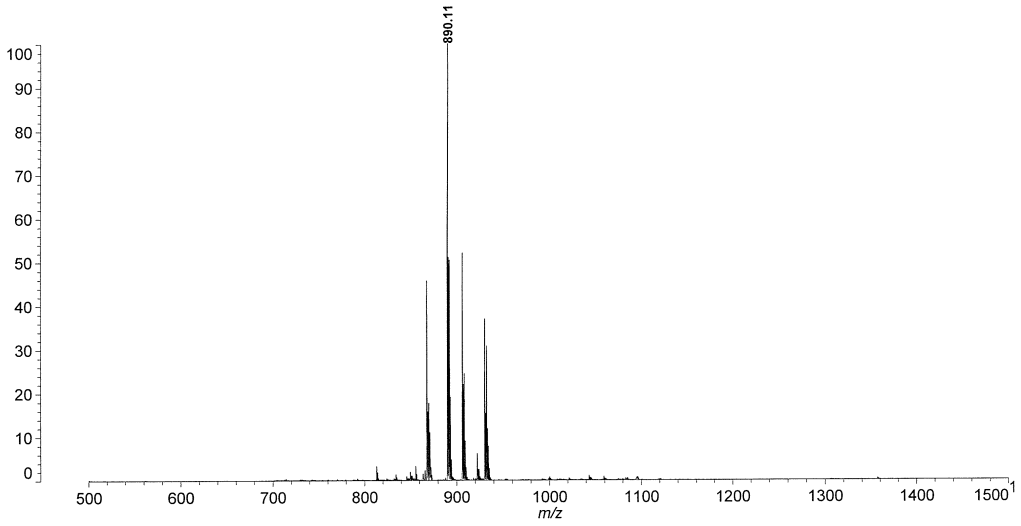

Figure S6. MALDI-TOF mass spectrum of **Cl-3F**. α-CHCA was used as a matrix. **Cl-3F**: calcd. $[M+Na]^+$ = 892.38 and obsd. $[M+Na]^+$ = 890.11.

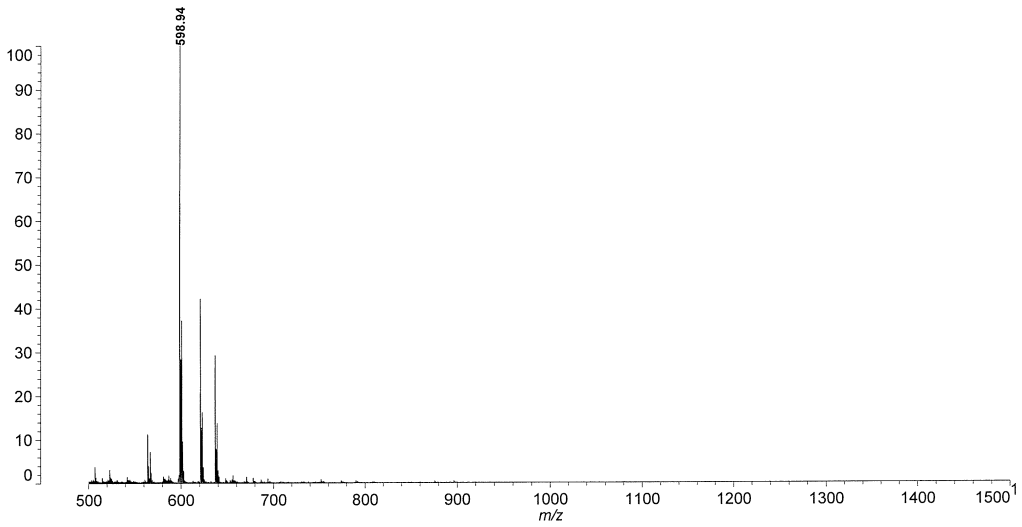

Figure S7. MALDI-TOF mass spectrum of **Cl-3G**. α-CHCA was used as a matrix. **Cl-3G**: calcd. $[M+H]^+$ = 600.27 and obsd. $[M+H]^+$ = 598.94.

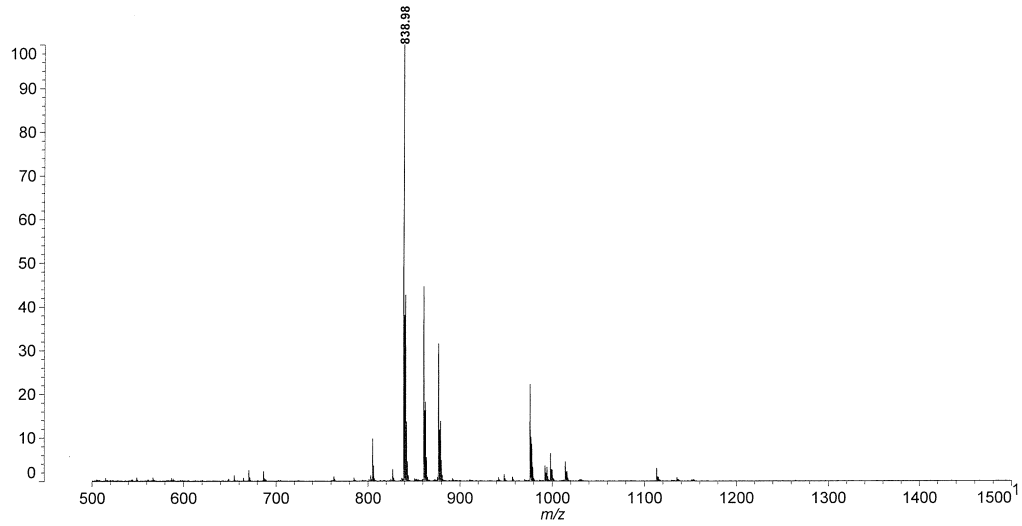

Figure S8. MALDI-TOF mass spectrum of **Cl-3H**. α-CHCA was used as a matrix. **Cl-3H**: calcd. $[M+H]^+$ = 840.38 and obsd. $[M+H]^+$ = 838.98.

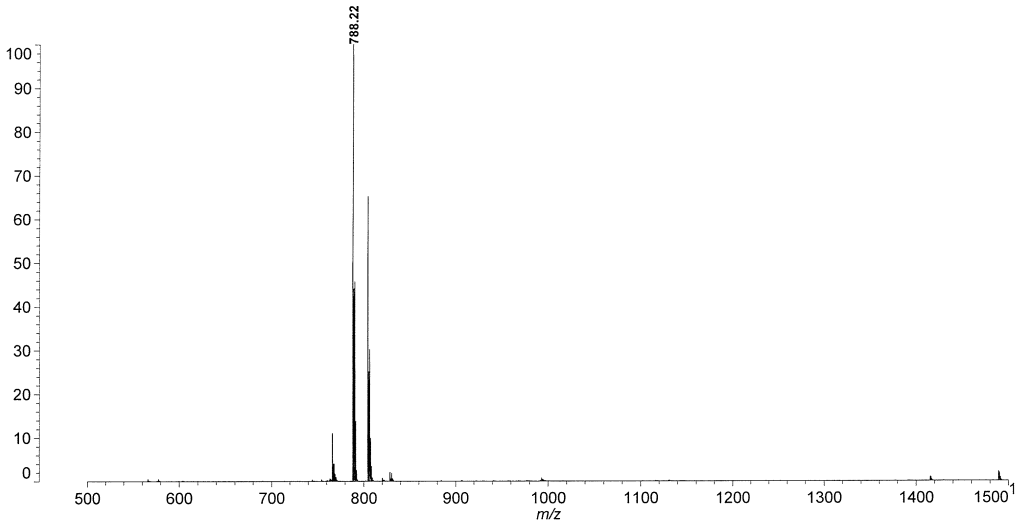

Figure S9. MALDI-TOF mass spectrum of **Cl-3I**. α-CHCA was used as a matrix. **Cl-3I**: calcd. $[M+Na]^+$ = 790.42 and obsd. $[M+Na]^+$ = 788.22.

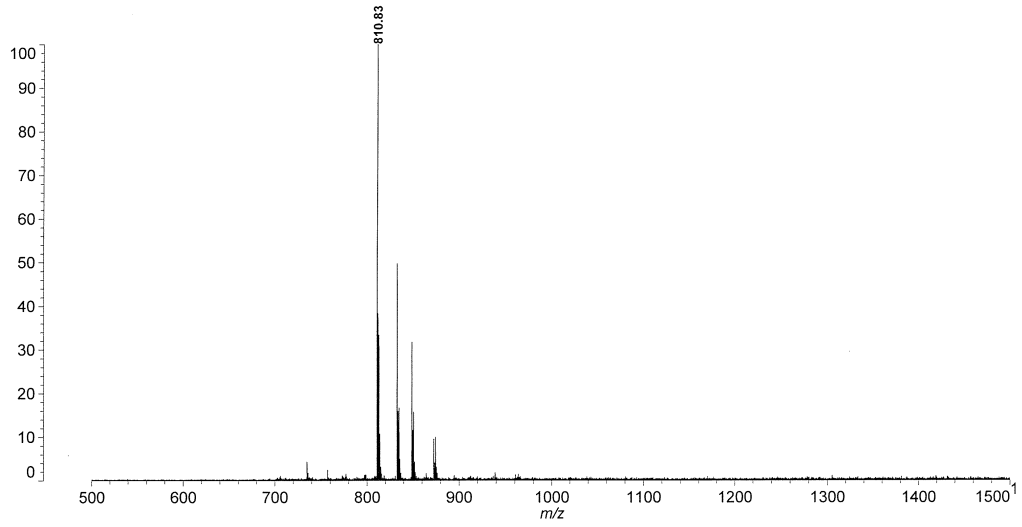

Figure S10. MALDI-TOF mass spectrum of **Cl-3K**. α-CHCA was used as a matrix. **Cl-3K**: calcd. $[M+H]^+$ = 813.49 and obsd. $[M+H]^+$ = 810.83.

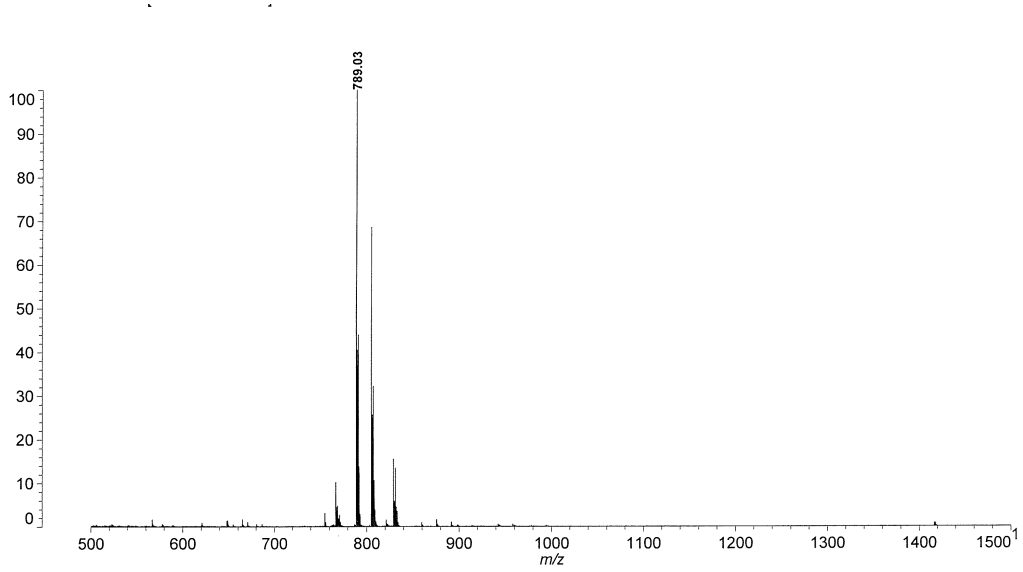

Figure S11. MALDI-TOF mass spectrum of **Cl-3L**. α-CHCA was used as a matrix. **Cl-3L**: calcd. $[M+Na]^+$ = 790.42 and obsd. $[M+Na]^+$ = 789.03.

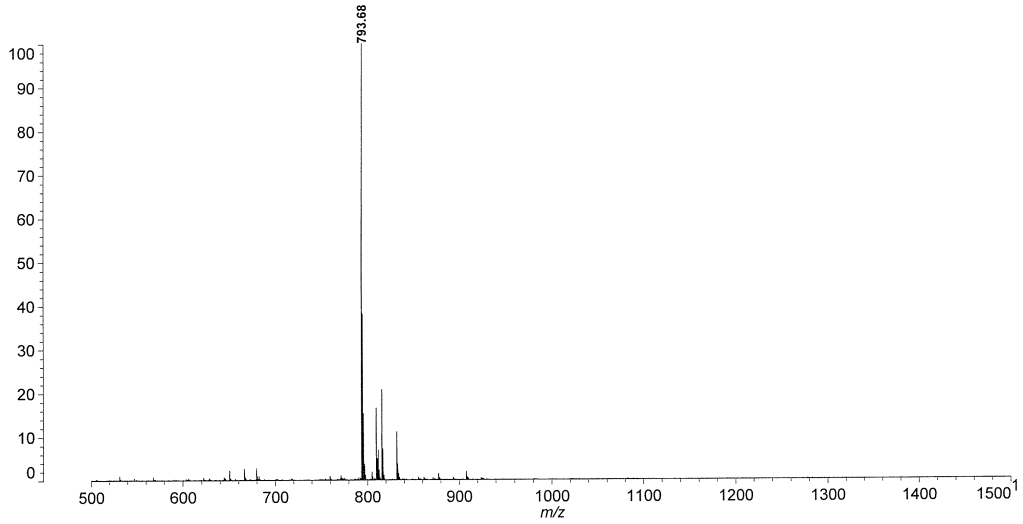

Figure S12. MALDI-TOF mass spectrum of **Cl-3N**. α-CHCA was used as a matrix. **Cl-3N**: calcd. $[M+Na]^+$ = 793.31 and obsd. $[M+Na]^+$ = 793.68.

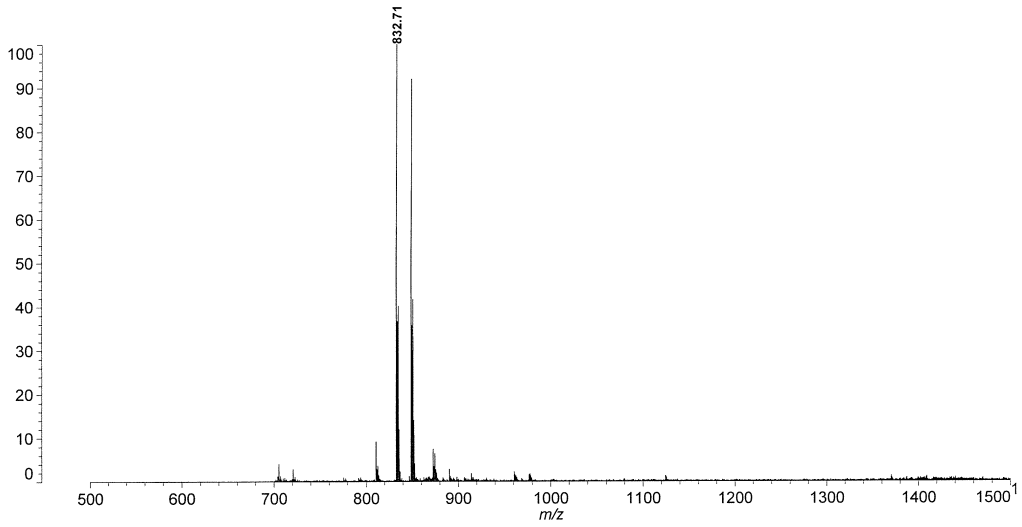

Figure S13. MALDI-TOF mass spectrum of **Cl-3Q**. α-CHCA was used as a matrix. **Cl-3Q**: calcd. $[M+Na]^+$ = 835.35 and obsd. $[M+Na]^+$ = 832.71.

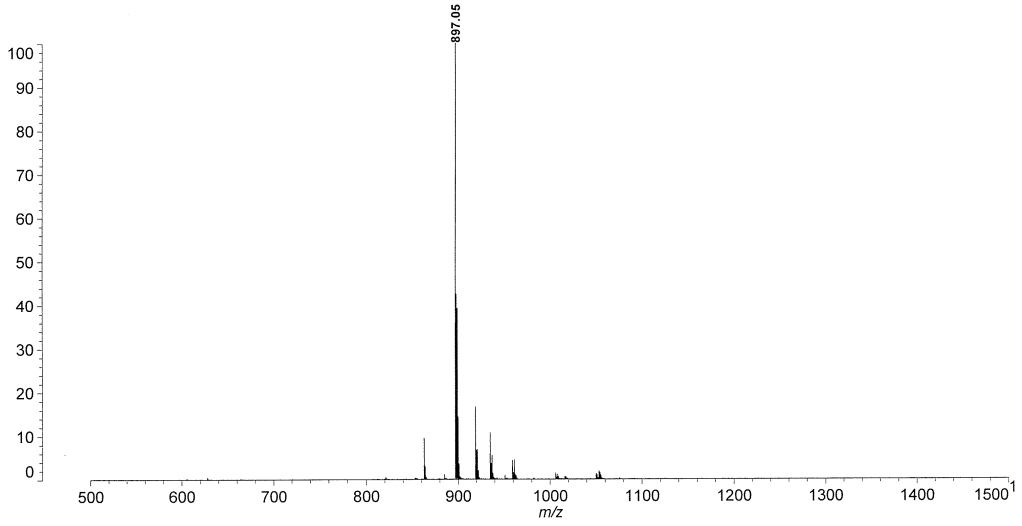

Figure S14. MALDI-TOF mass spectrum of **Cl-3R**. α-CHCA was used as a matrix. **Cl-3R**: calcd. $[M+H]^+$ = 898.48 and obsd. $[M+H]^+$ = 897.05.

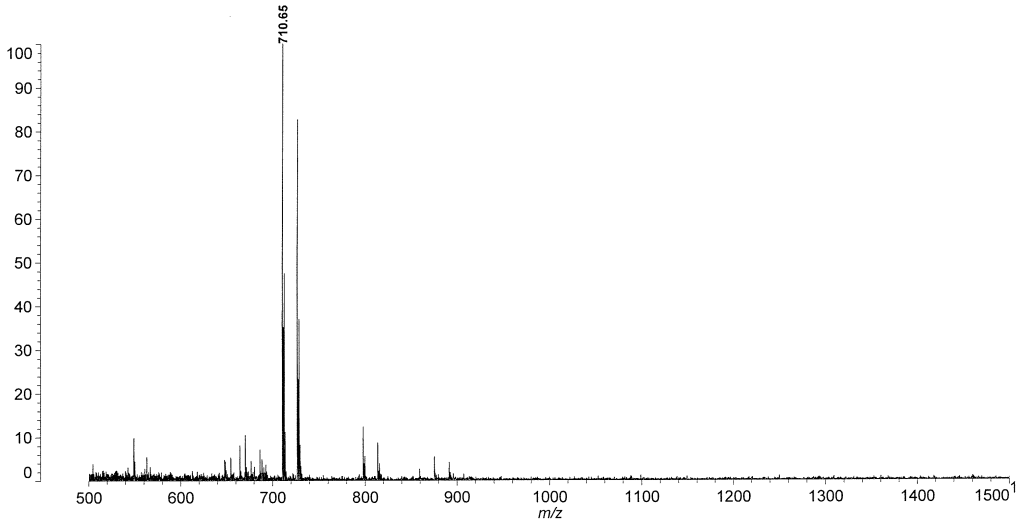

Figure S15. MALDI-TOF mass spectrum of **Cl-3S**. α-CHCA was used as a matrix. **Cl-3S**: calcd. $[M+H]^+$ = 712.28 and obsd. $[M+H]^+$ = 710.65.

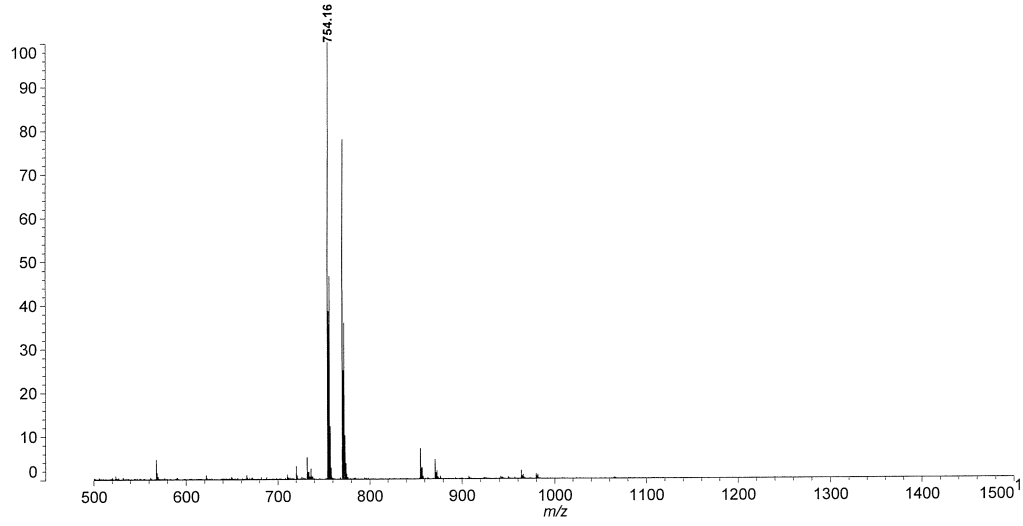

Figure S16. MALDI-TOF mass spectrum of **Cl-3T**. α-CHCA was used as a matrix. **Cl-3T**: calcd. $[M+Na]^+$ = 754.32 and obsd. $[M+Na]^+$ = 754.16.

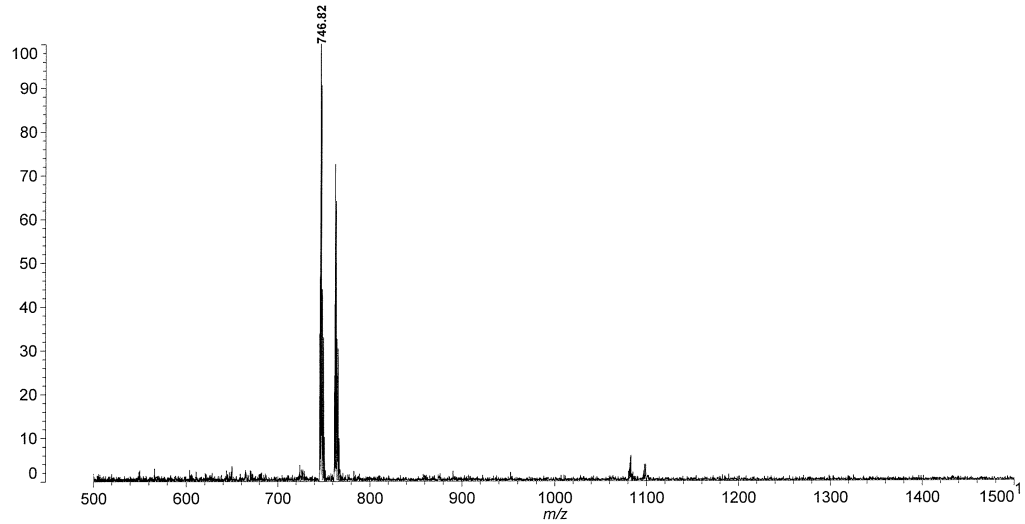

Figure S17. MALDI-TOF mass spectrum of **Cl-3V**. α-CHCA was used as a matrix. **Cl-3V**: calcd. $[M+Na]^+$ = 748.39 and obsd. $[M+Na]^+$ = 746.82.

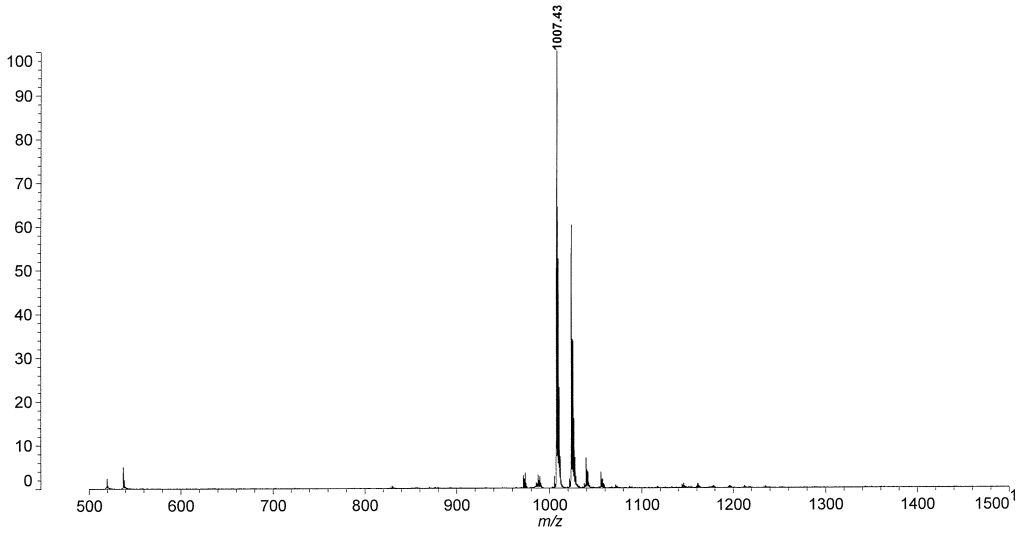

Figure S18. MALDI-TOF mass spectrum of **Cl-3W**. α-CHCA was used as a matrix. **Cl-3W**: calcd. $[M+H]^+$ = 1009.42 and obsd. $[M+H]^+$ = 1007.43.

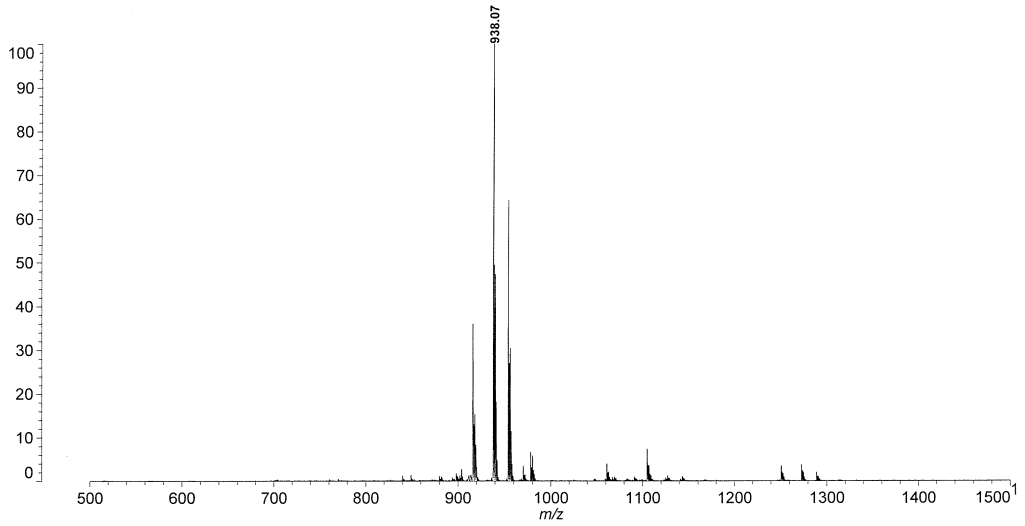

Figure S19. MALDI-TOF mass spectrum of **Cl-3Y**. α-CHCA was used as a matrix. **Cl-3Y**: calcd. $[M+H]^+$ = 940.36 and obsd. $[M+H]^+$ = 938.07.

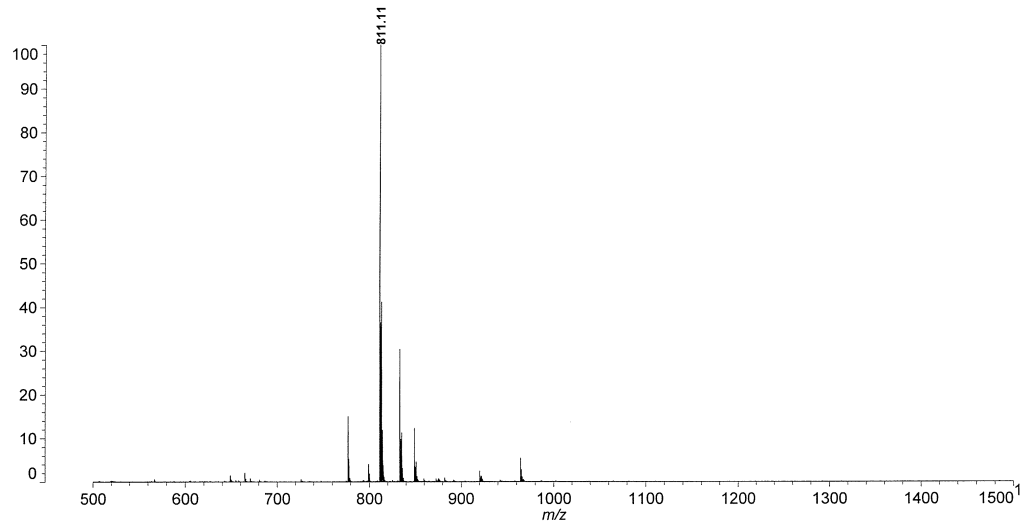

Figure S20. MALDI-TOF mass spectrum of **Cl-2R**. α-CHCA was used as a matrix. **Cl-2R**: calcd. $[M+H]^+$ = 812.44 and obsd. $[M+H]^+$ = 811.11.

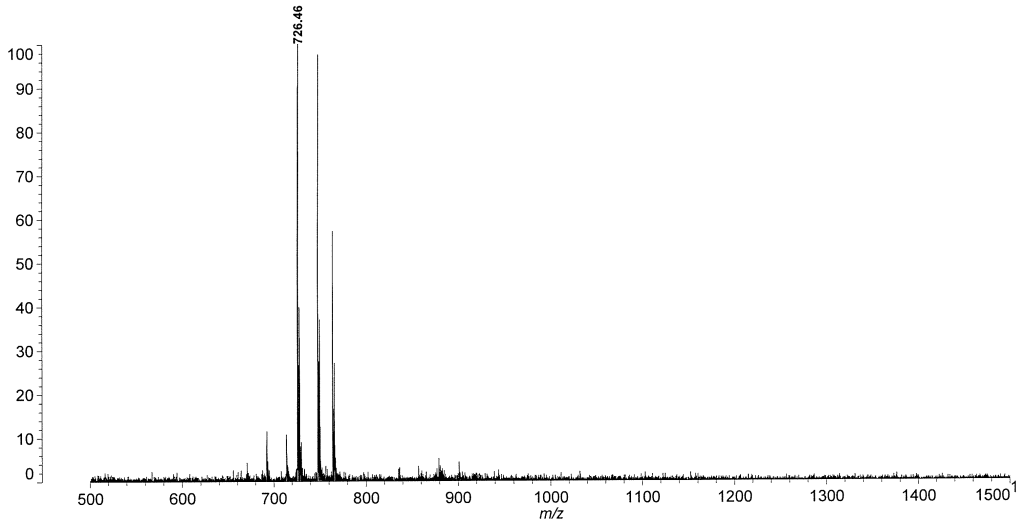

Figure S21. MALDI-TOF mass spectrum of **Cl-1R**. α-CHCA was used as a matrix. **Cl-1R**: calcd. $[M+H]^+$ = 727.38 and obsd. $[M+H]^+$ = 726.46.

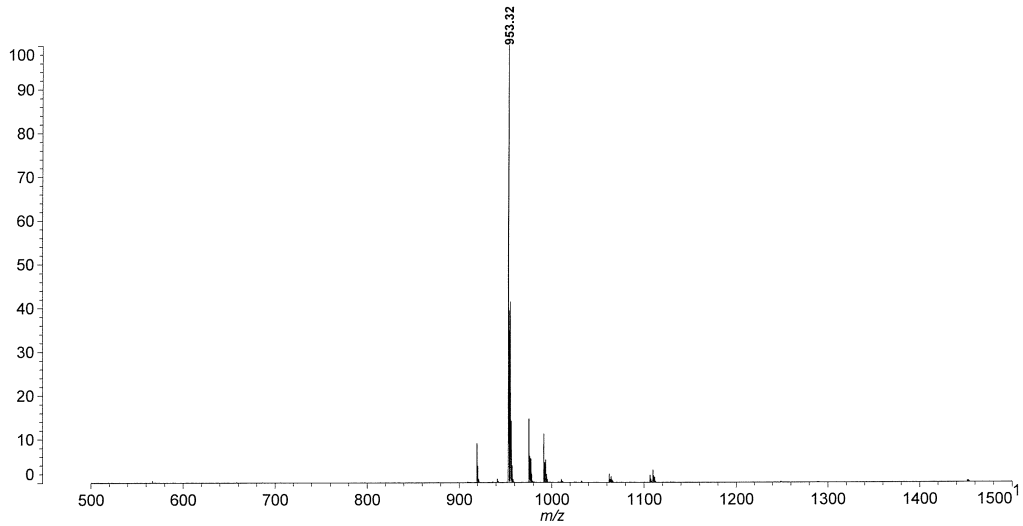

Figure S22. MALDI-TOF mass spectrum of **Cl-C1-3R**. α-CHCA was used as a matrix. **Cl-C1-3R**: calcd. $[M+H]^+$ = 954.53 and obsd. $[M+H]^+$ = 953.32.

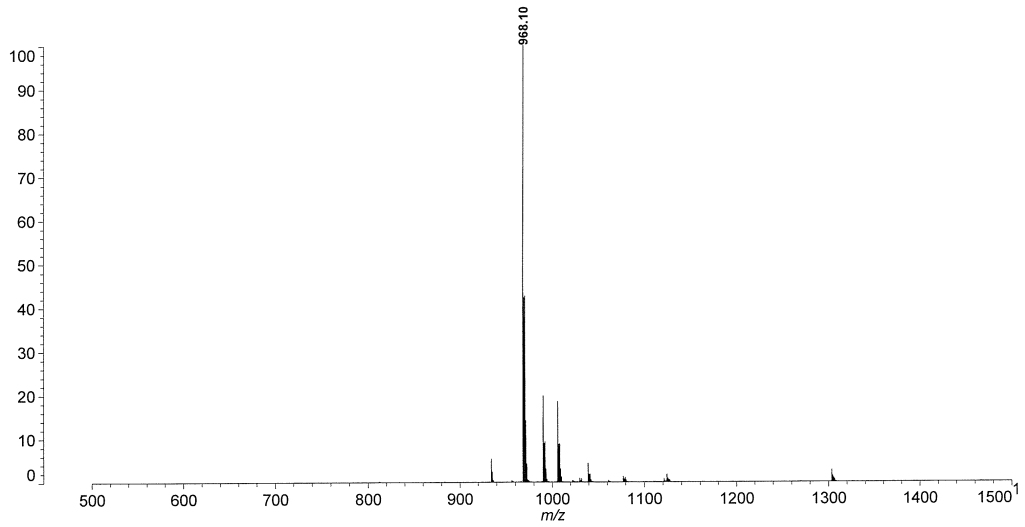

Figure S23. MALDI-TOF mass spectrum of **Cl-C2-3R**. α-CHCA was used as a matrix. **Cl-C2-3R**: calcd. $[M+H]^+$ = 968.54 and obsd. $[M+H]^+$ = 968.10.

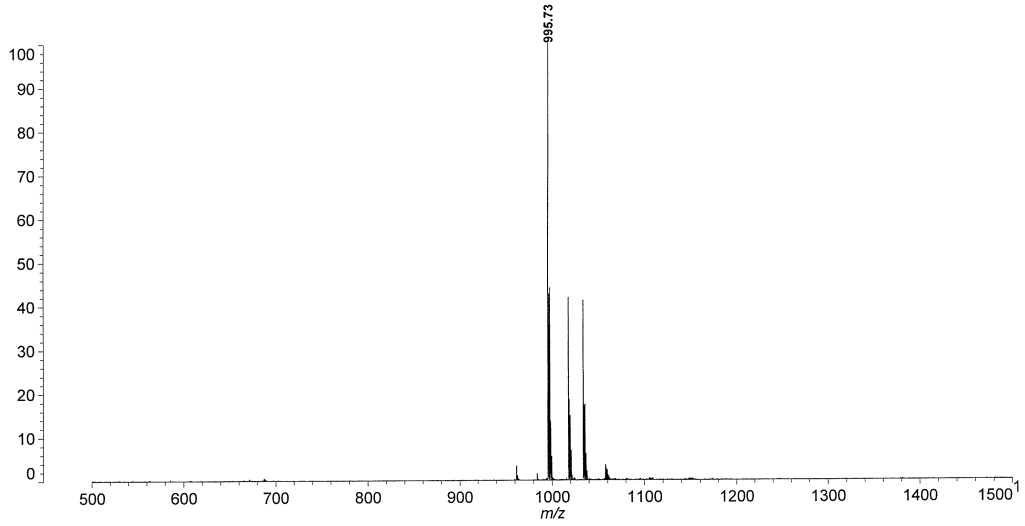

Figure S24. MALDI-TOF mass spectrum of **Cl-C4-3R**. α-CHCA was used as a matrix. **Cl-C4-3R**: calcd. $[M+H]^+$ = 996.57 and obsd. $[M+H]^+$ = 995.73.

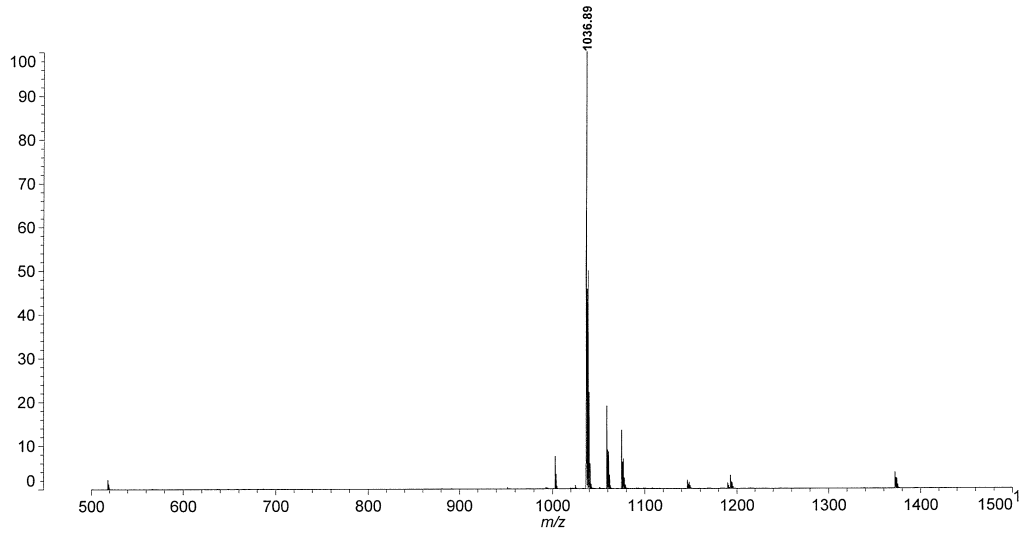

Figure S25. MALDI-TOF mass spectrum of **Cl-C7-3R**. α-CHCA was used as a matrix. **Cl-C7-3R**: calcd. $[M+H]^+$ = 1038.62 and obsd. $[M+H]^+$ = 1036.89.

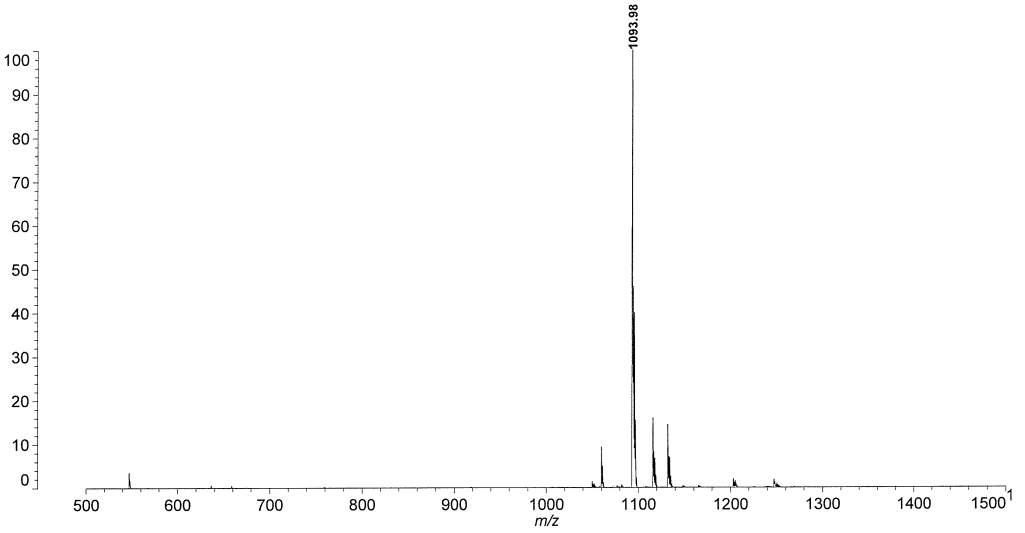

Figure S26. MALDI-TOF mass spectrum of **Cl-C11-3R**. α-CHCA was used as a matrix. **Cl-C11-3R**: calcd. $[M+H]^+$ = 1095.81 and obsd. $[M+H]^+$ = 1093.98.

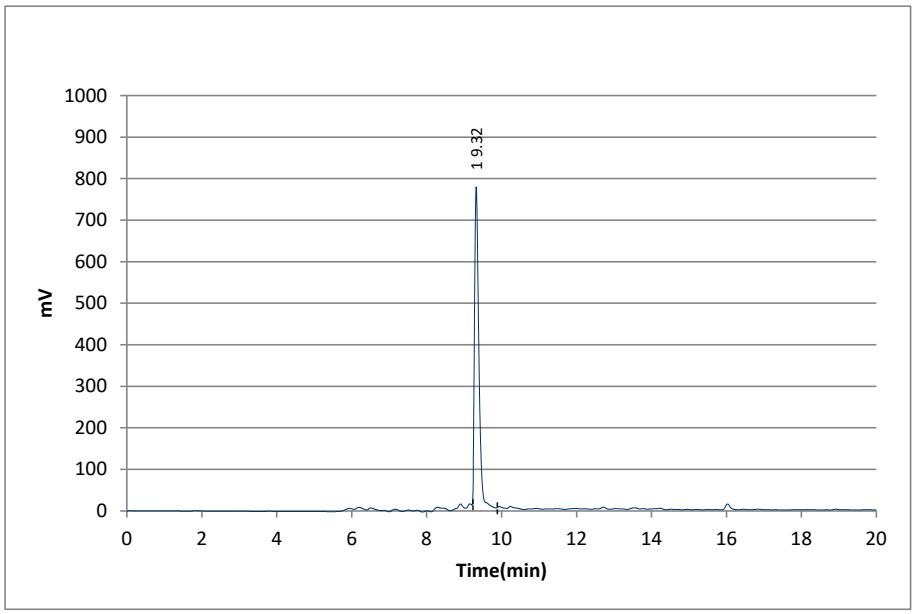

Figure S27. HPLC chromatogram of **Cl-3A**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

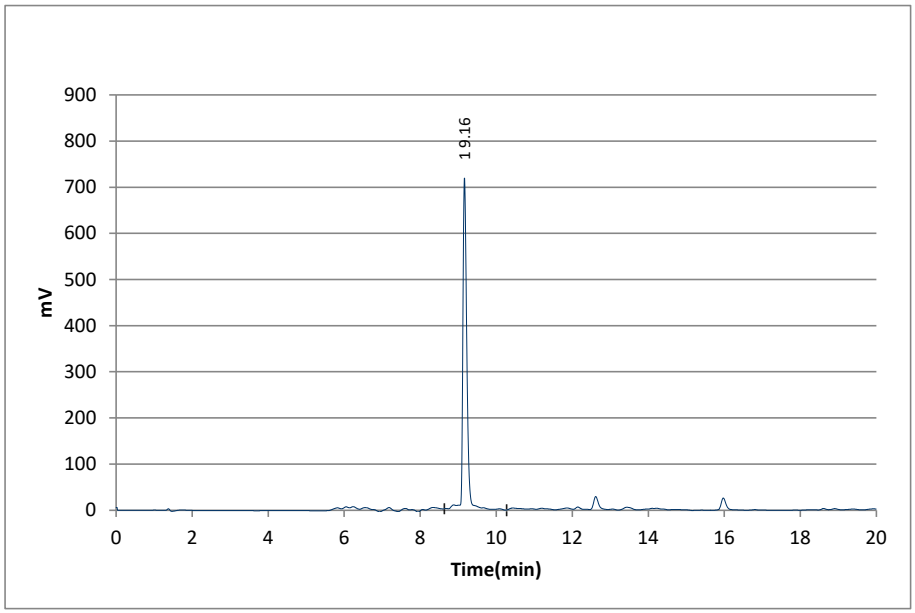

Figure S28. HPLC chromatogram of **Cl-3D**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

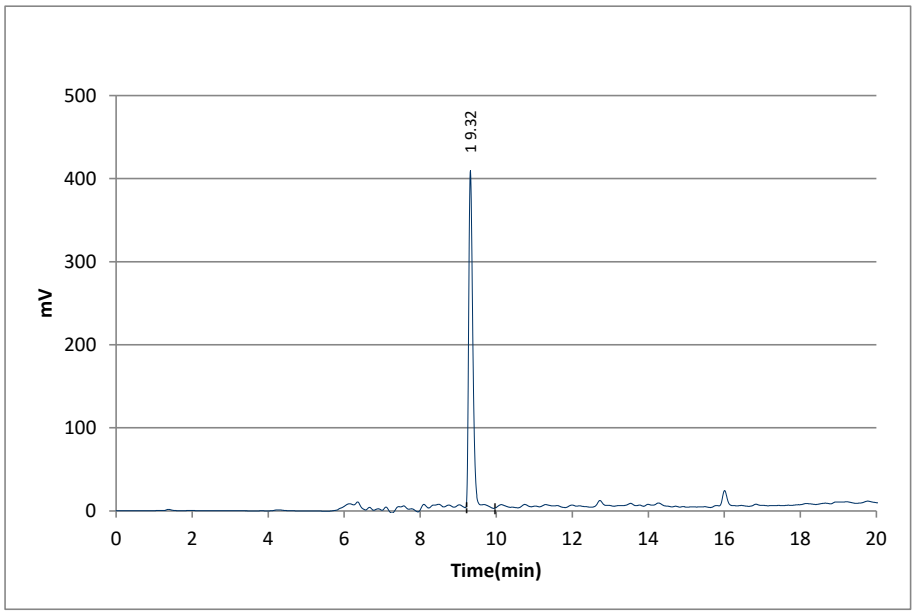

Figure S29. HPLC chromatogram of **Cl-3E**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

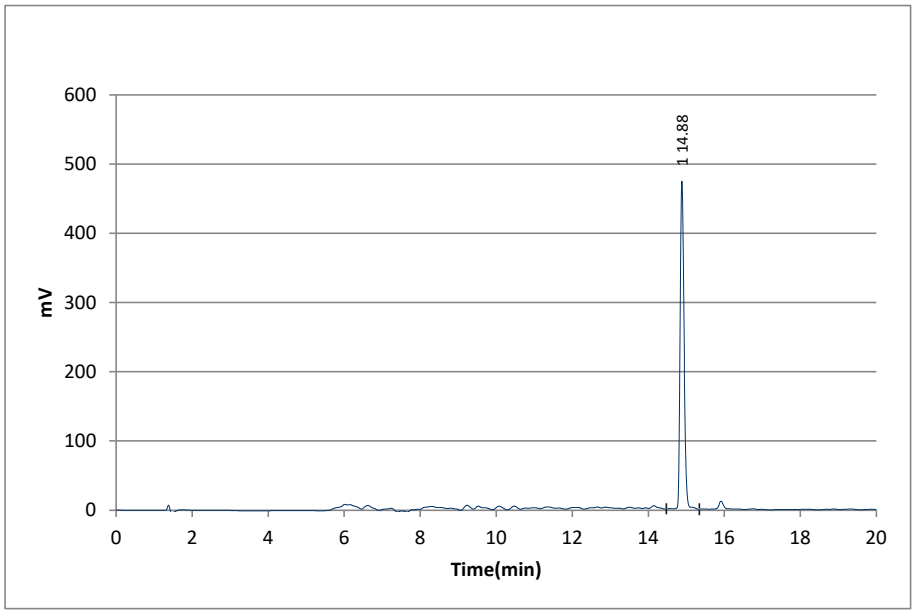

Figure S30. HPLC chromatogram of **Cl-3F**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

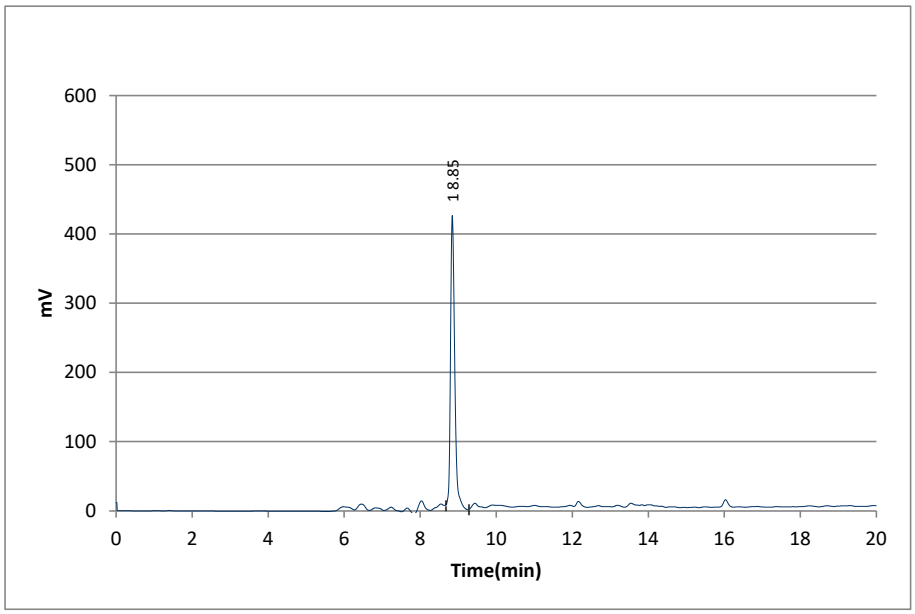

Figure S31. HPLC chromatogram of **Cl-3G**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

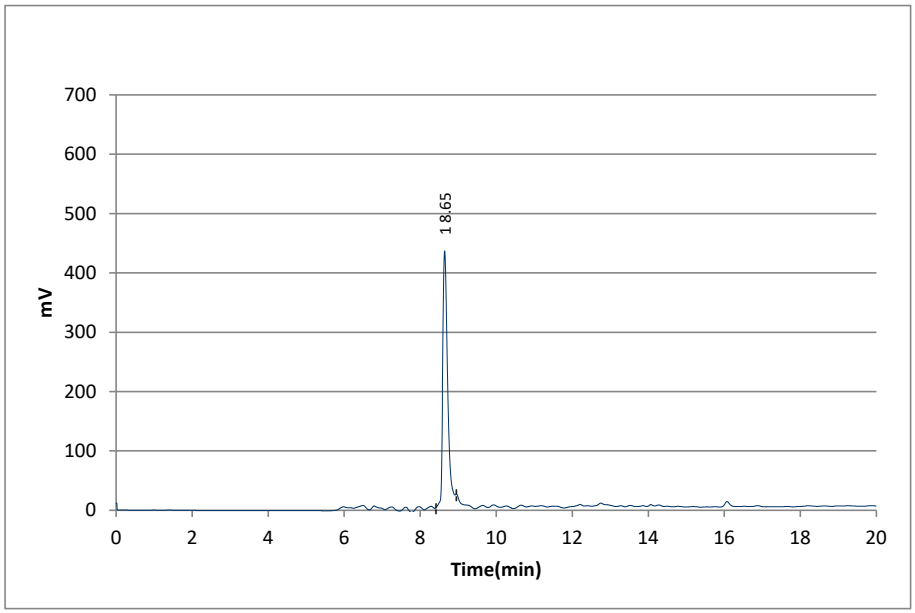

Figure S32. HPLC chromatogram of **Cl-3H**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

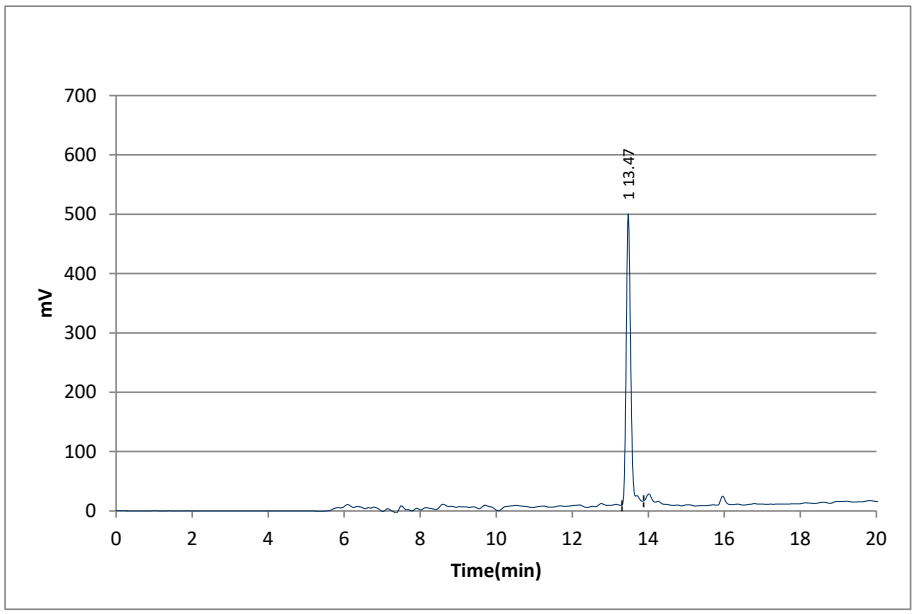

Figure S33. HPLC chromatogram of **Cl-3I**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

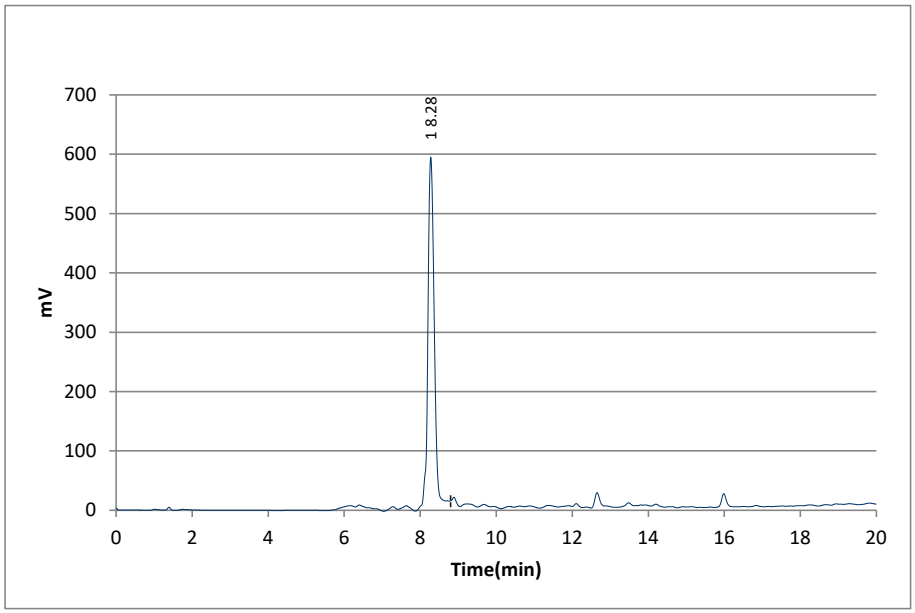

Figure S34. HPLC chromatogram of **Cl-3K**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

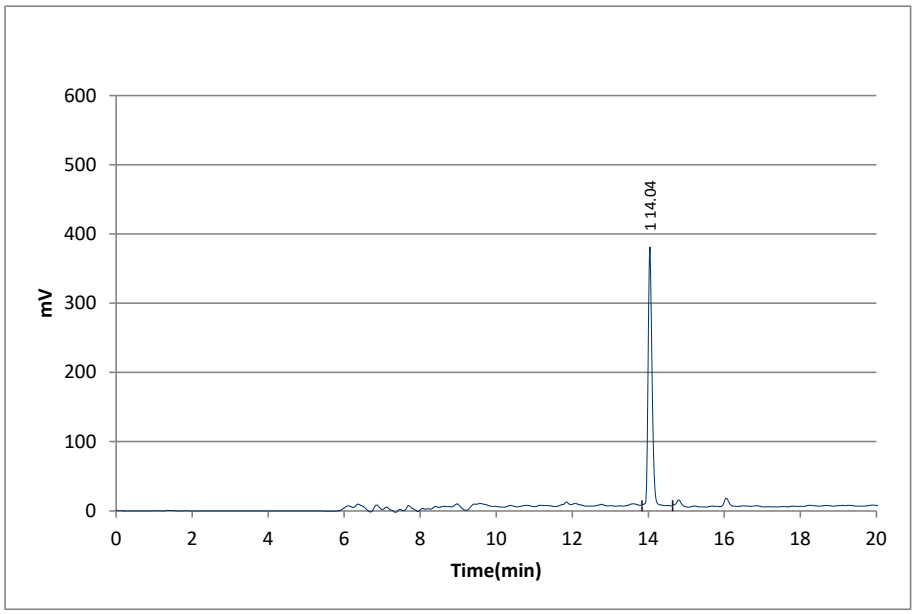

Figure S35. HPLC chromatogram of **Cl-3L**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

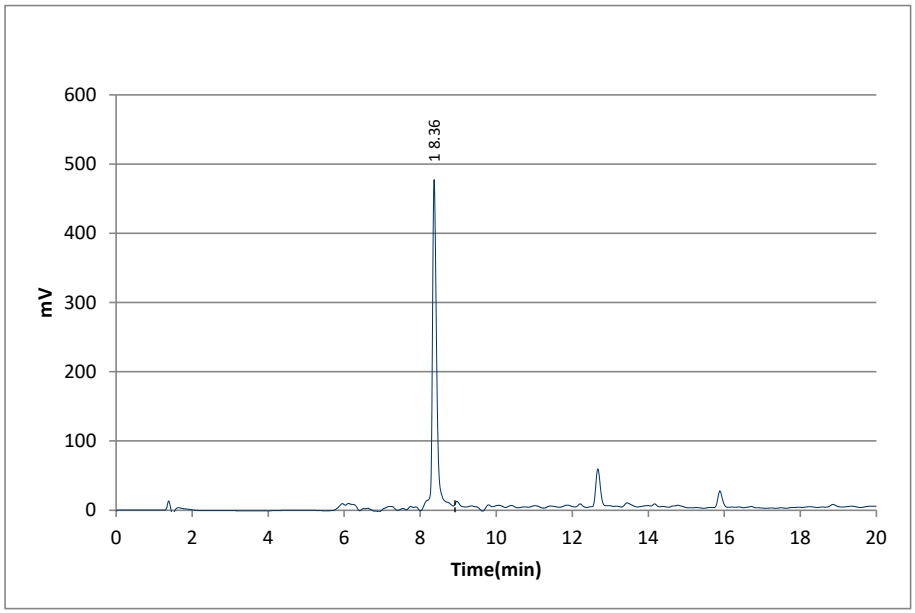

Figure S36. HPLC chromatogram of **Cl-3N**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

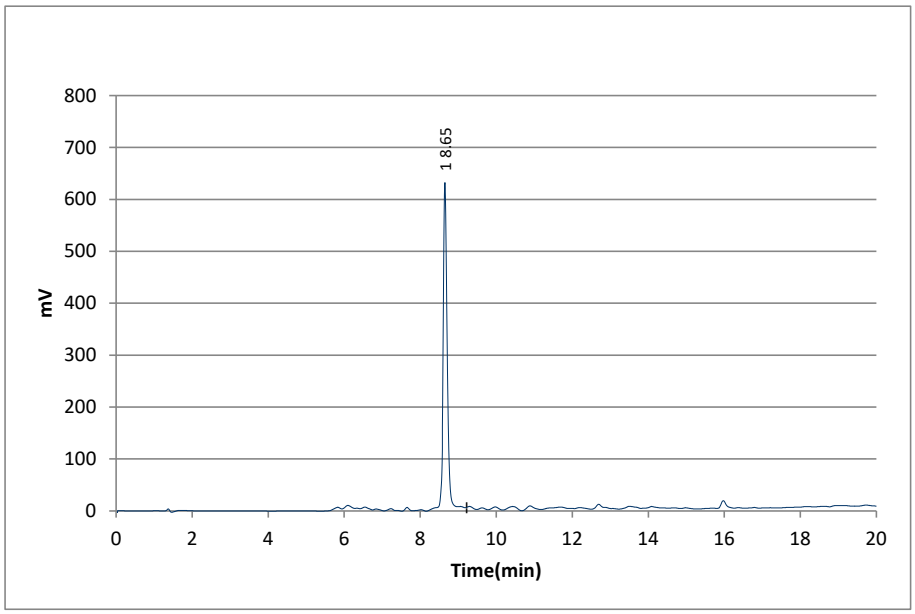

Figure S37. HPLC chromatogram of **Cl-3Q**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

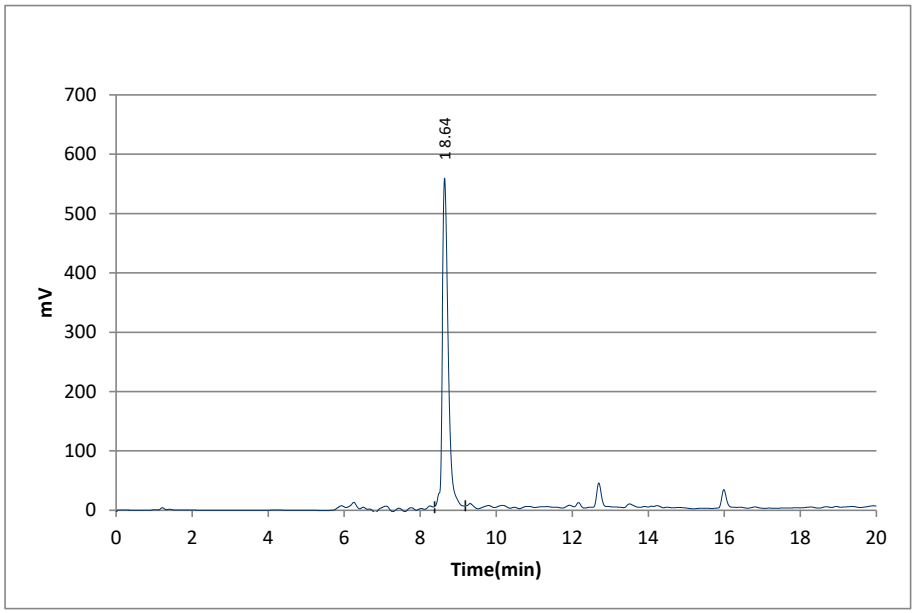

Figure S38. HPLC chromatogram of **Cl-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

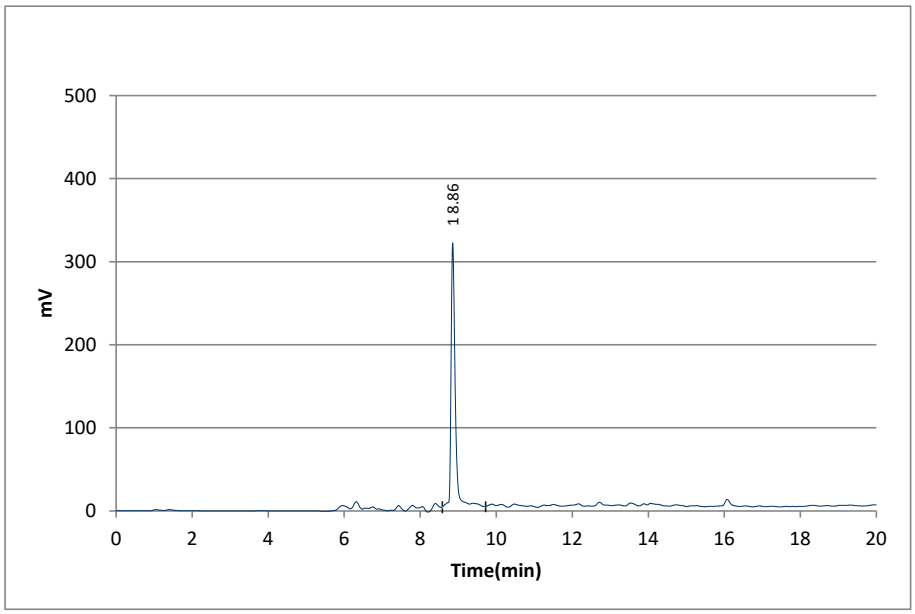

Figure S39. HPLC chromatogram of **Cl-3S**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

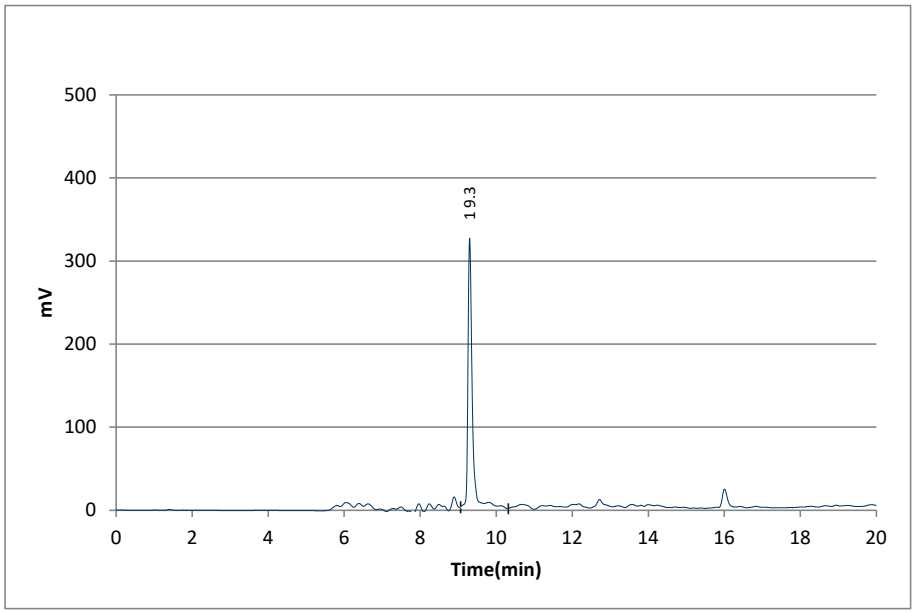

Figure S40. HPLC chromatogram of **Cl-3T**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

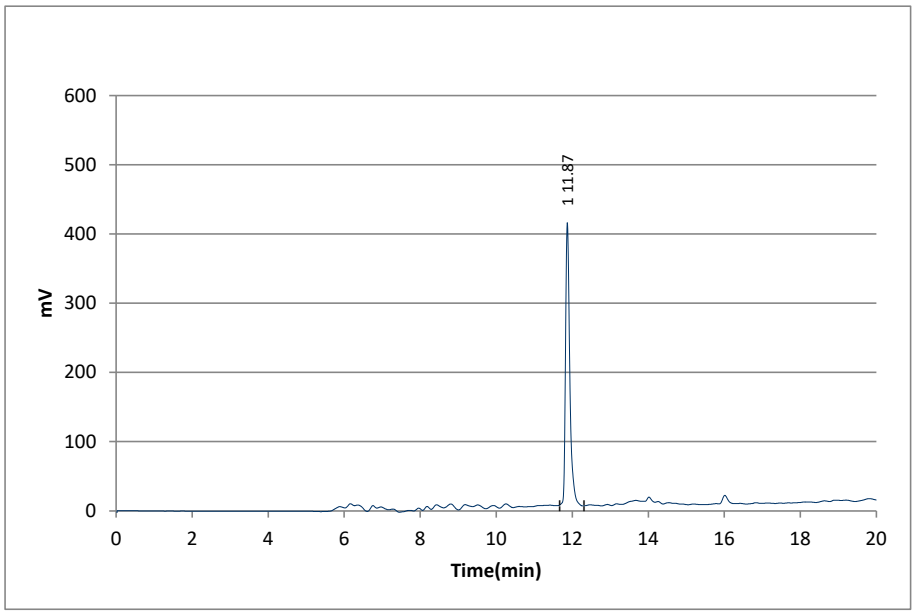

Figure S41. HPLC chromatogram of **Cl-3V**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

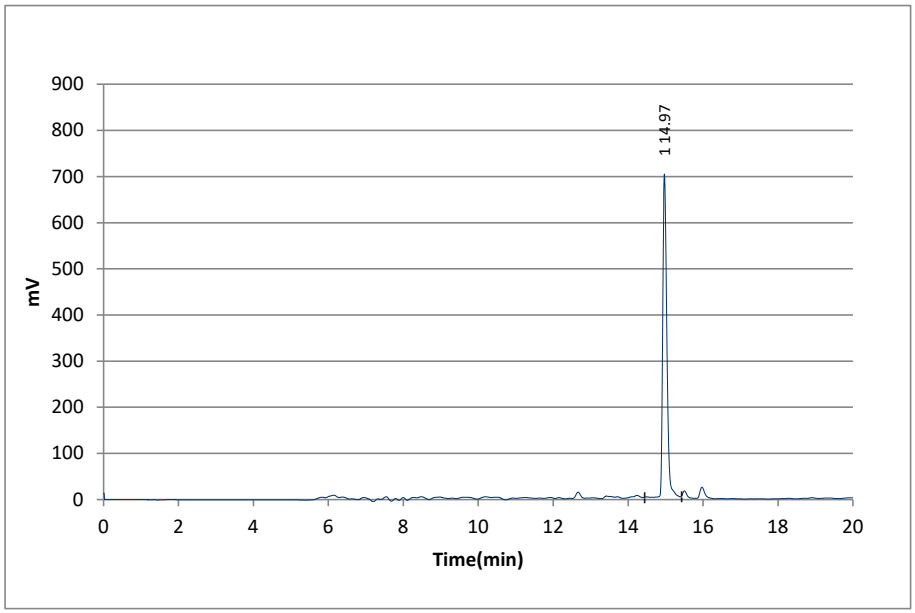

Figure S42. HPLC chromatogram of **Cl-3W**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

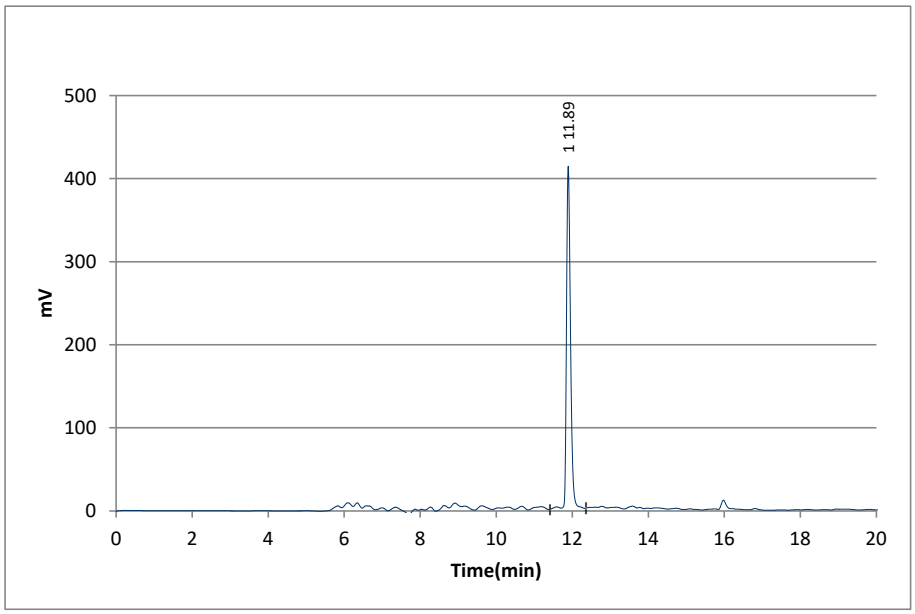

Figure S43. HPLC chromatogram of **Cl-3Y**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

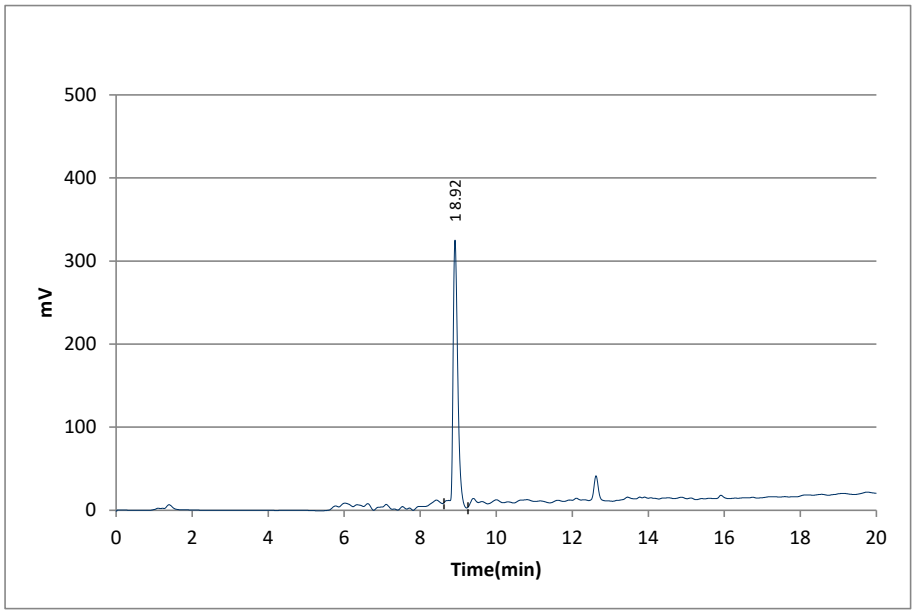

Figure S44. HPLC chromatogram of **Cl-2R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

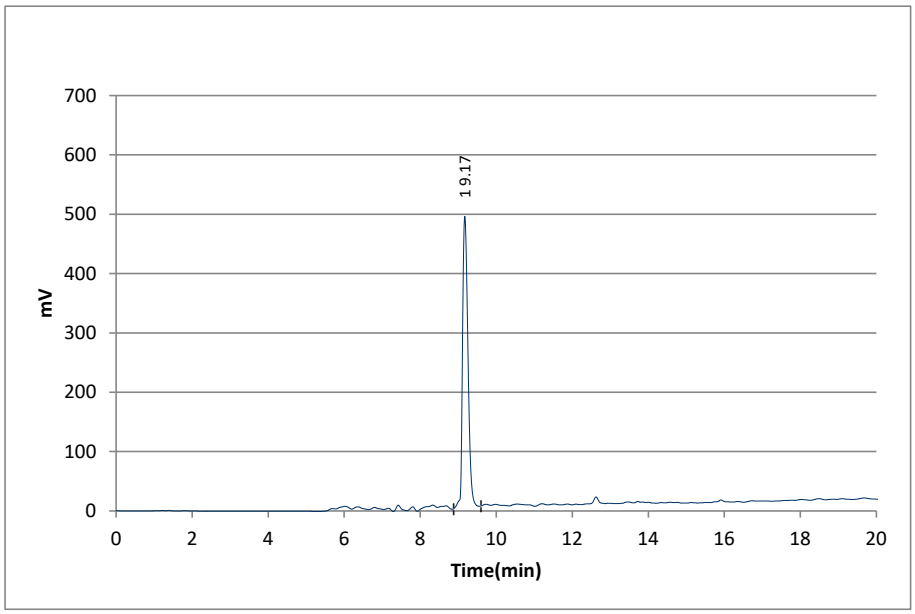

Figure S45. HPLC chromatogram of **Cl-1R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

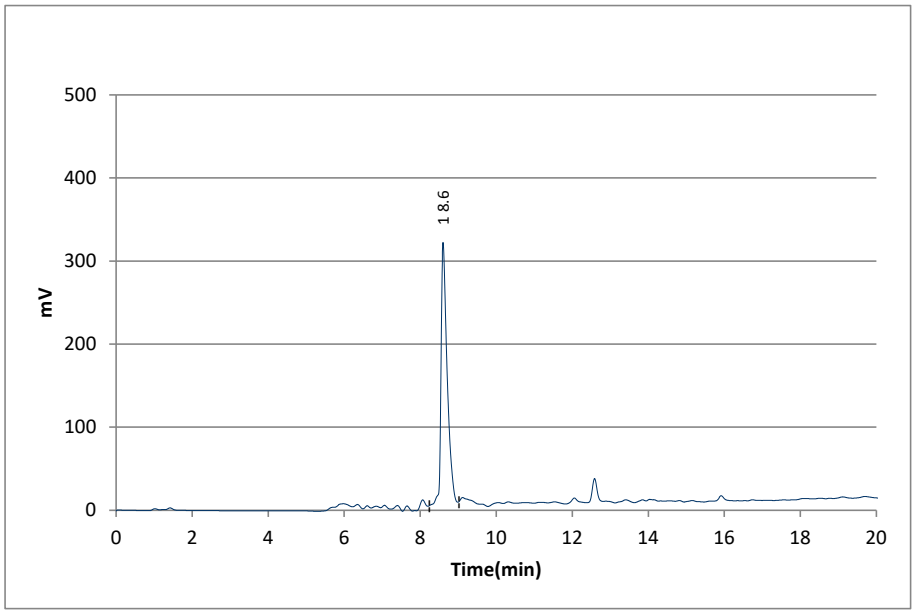

Figure S46. HPLC chromatogram of **Cl-C1-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

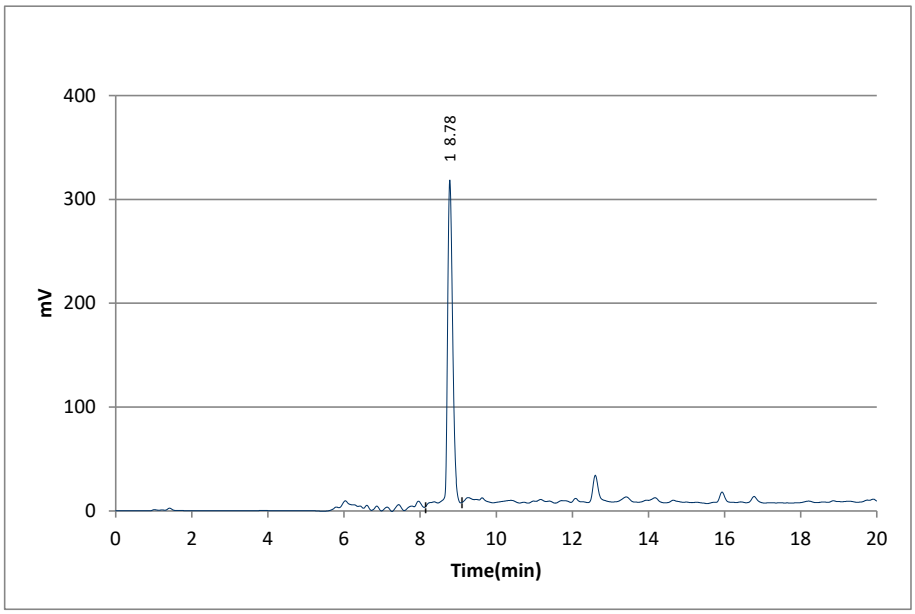

Figure S47. HPLC chromatogram of **Cl-C2-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

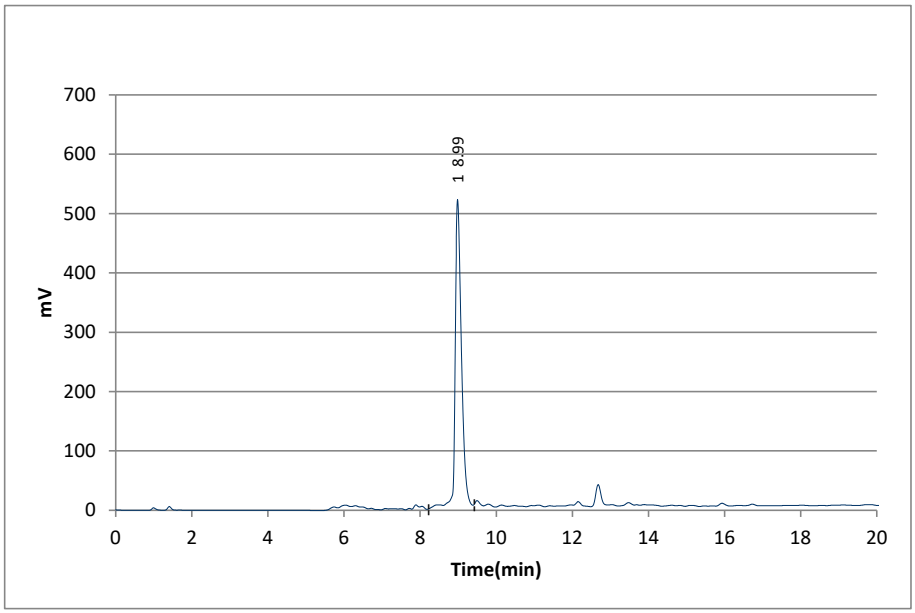

Figure S48. HPLC chromatogram of **Cl-C4-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

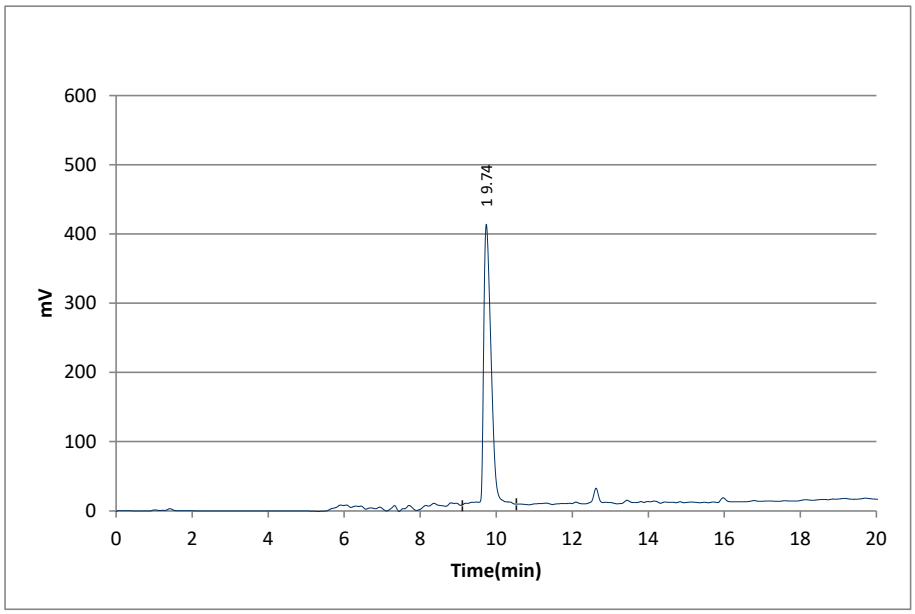

Figure S49. HPLC chromatogram of **Cl-C7-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

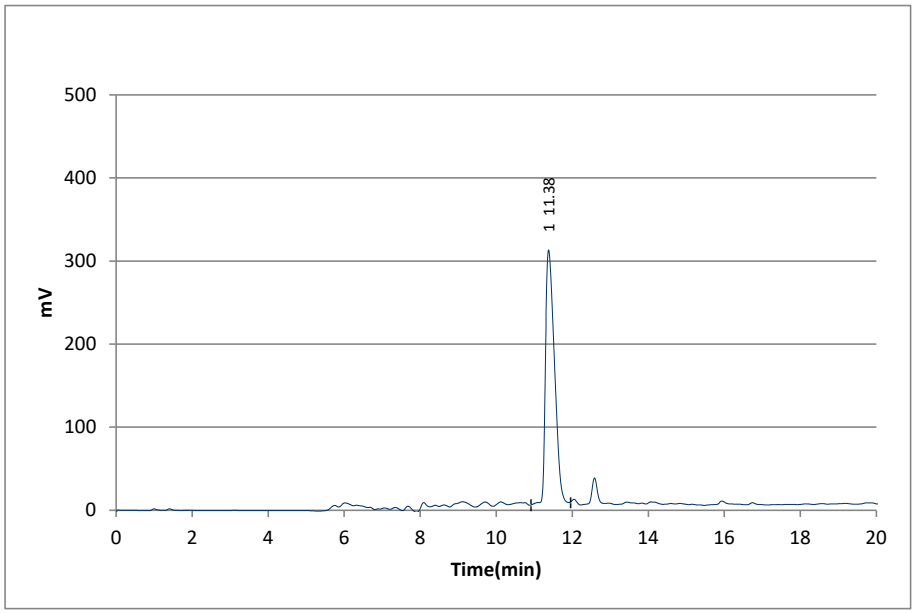

Figure S50. HPLC chromatogram of **Cl-C11-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

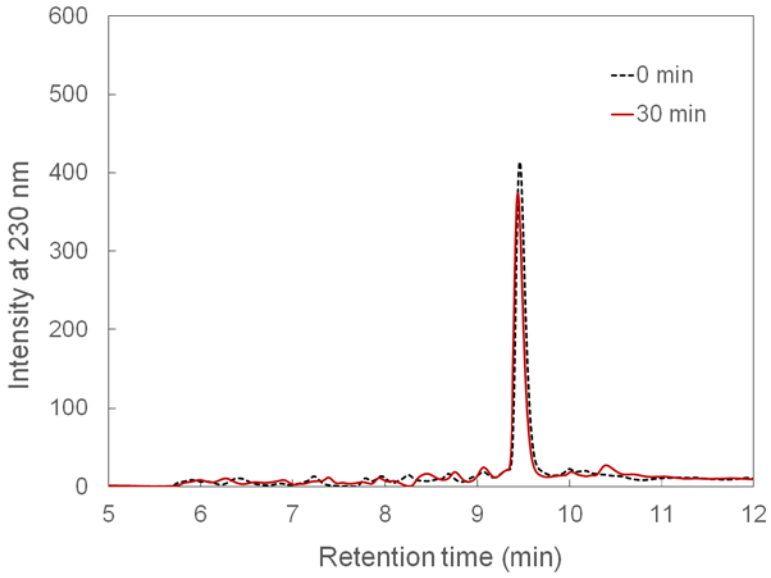

Figure S51. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3A** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

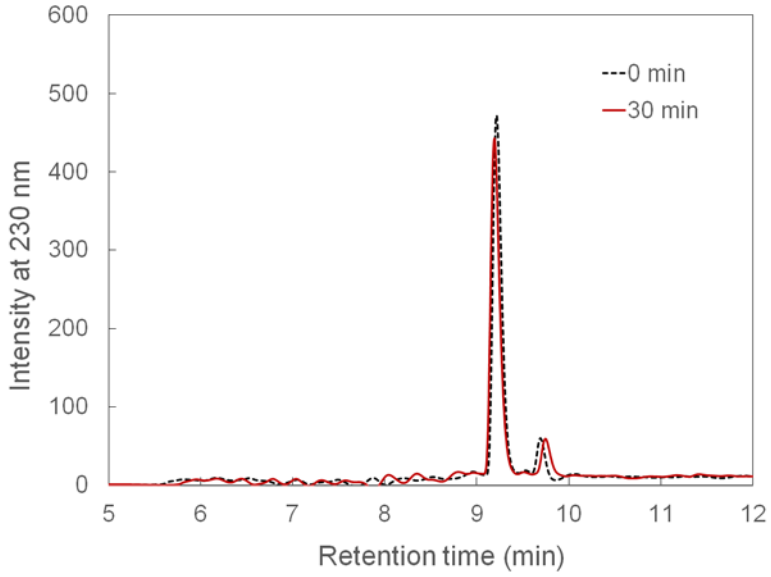

Figure S52. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3D** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

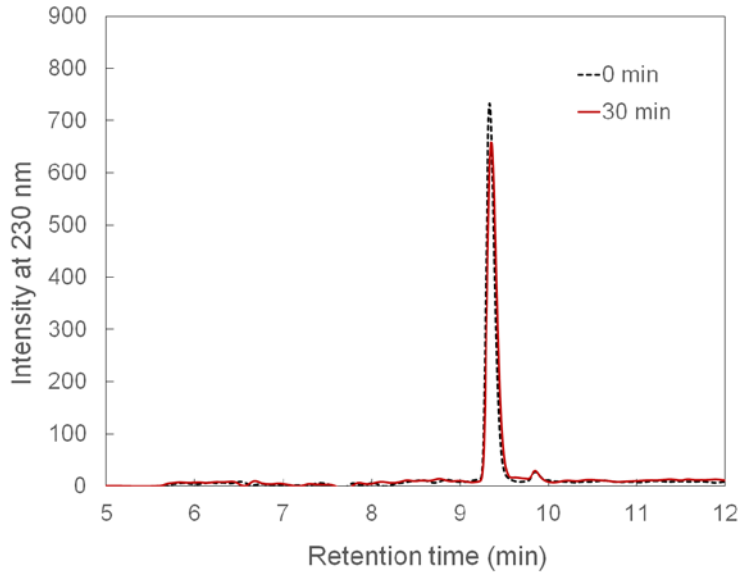

Figure S53. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3E** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

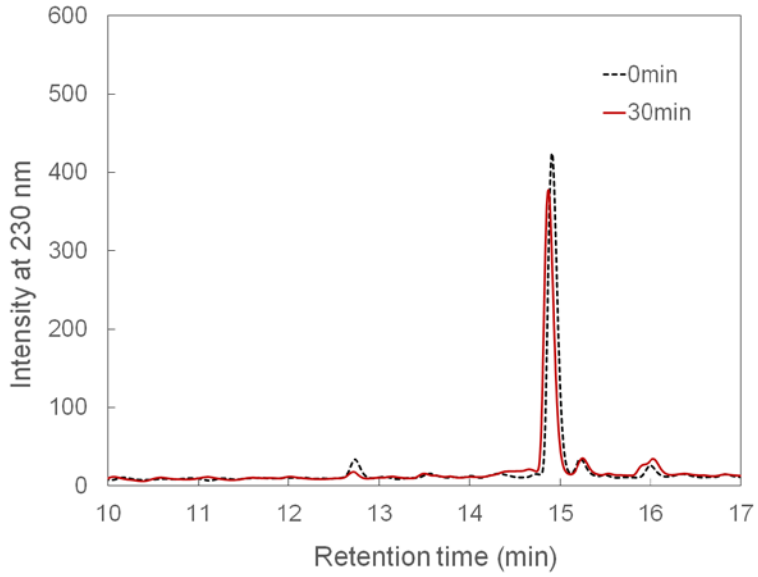

Figure S54. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3F** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

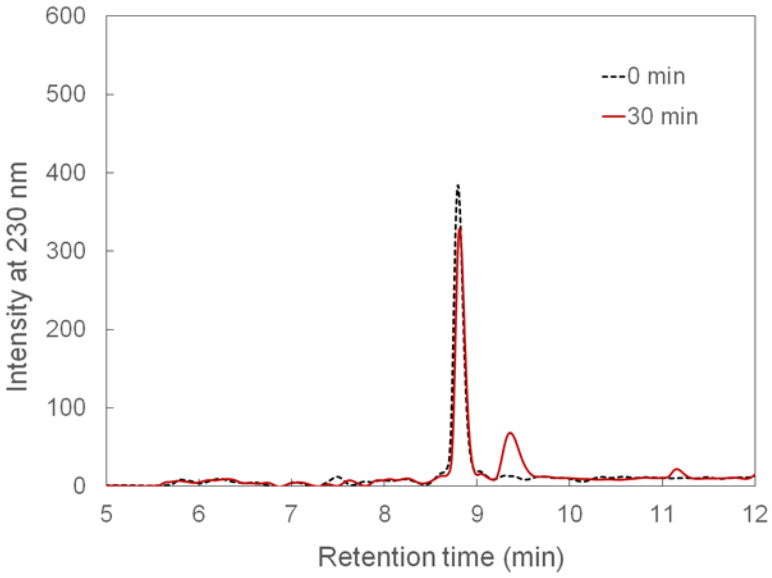

Figure S55. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3G** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

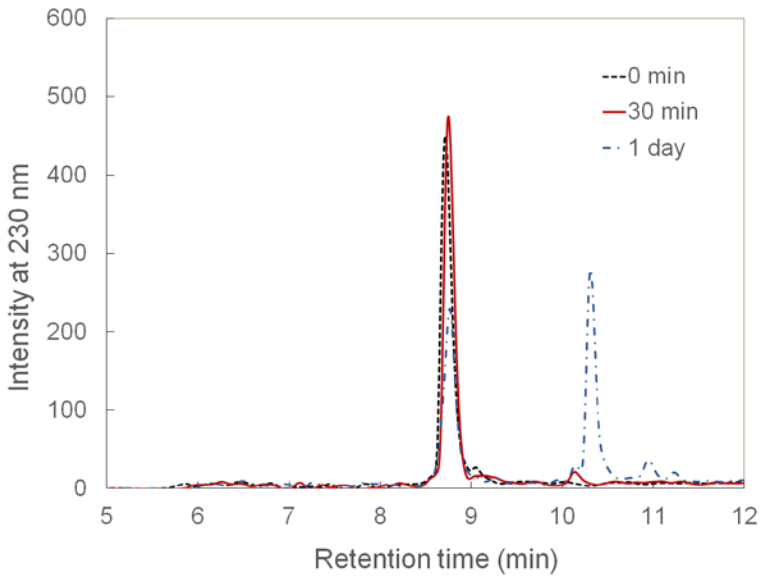

Figure S56. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3H** after 0 and 30 min, and 1 day. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

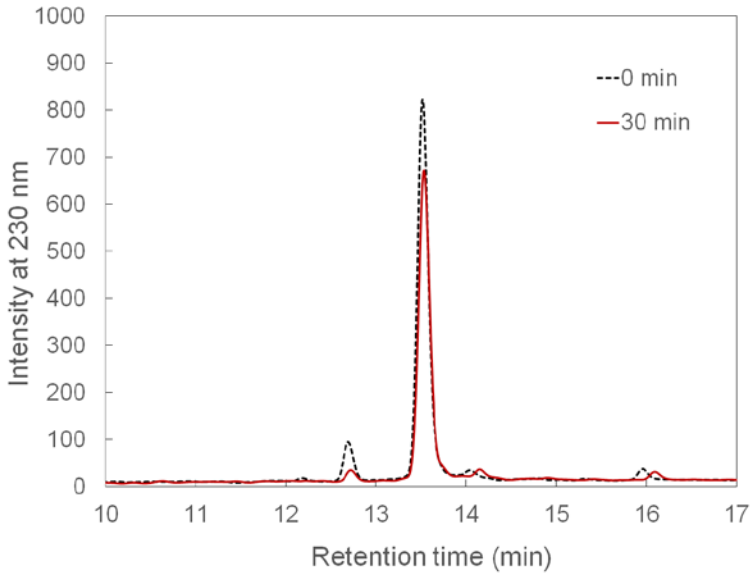

Figure S57. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3I** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

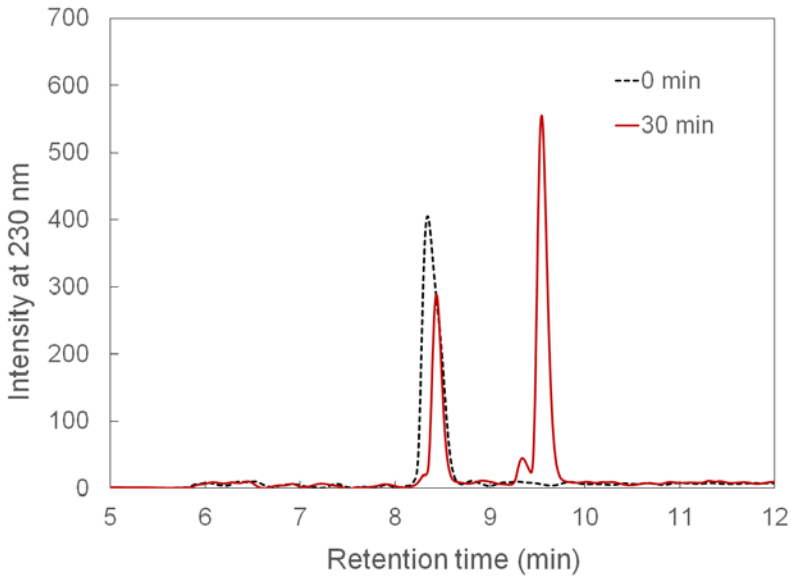

Figure S58. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3K** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

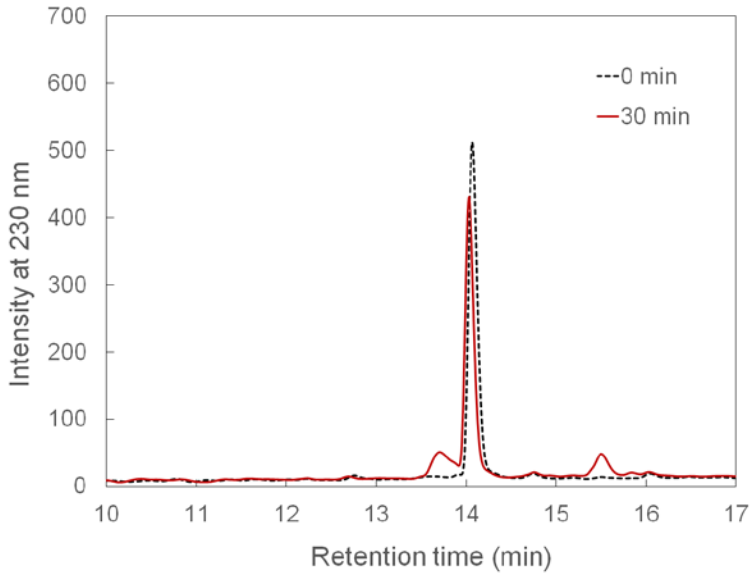

Figure S59. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3L** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

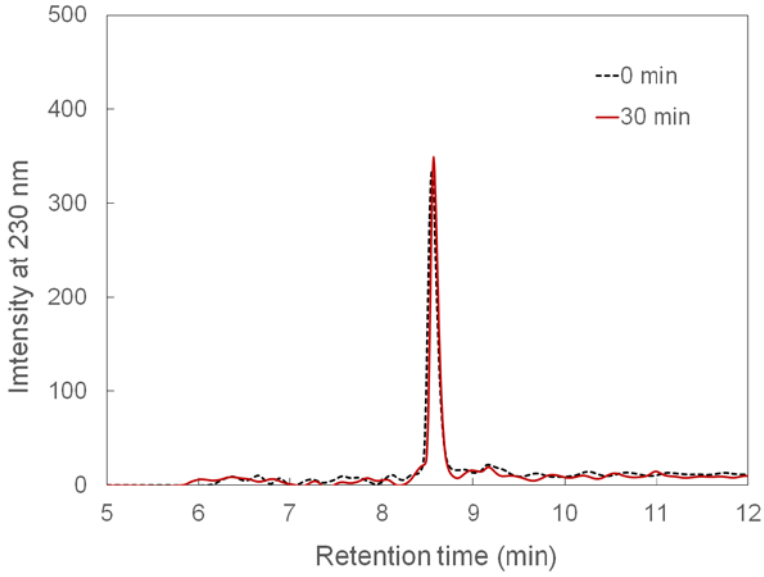

Figure S60. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3N** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

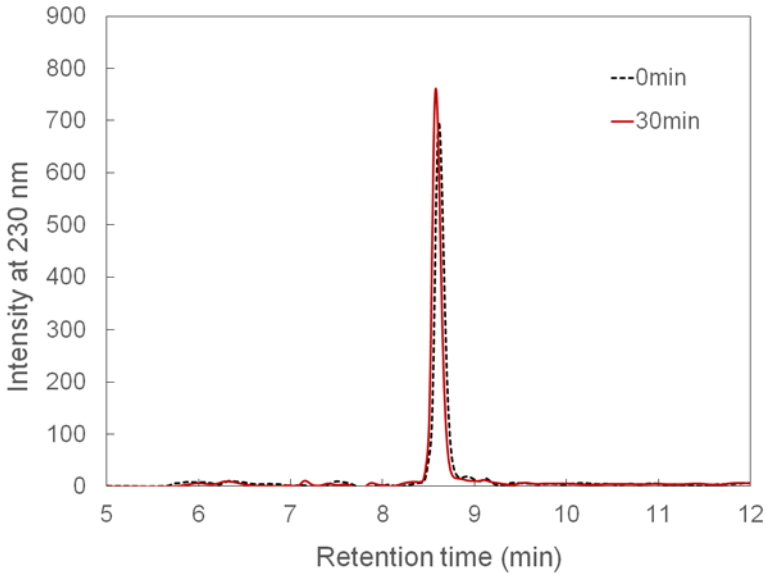

Figure S61. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3Q** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

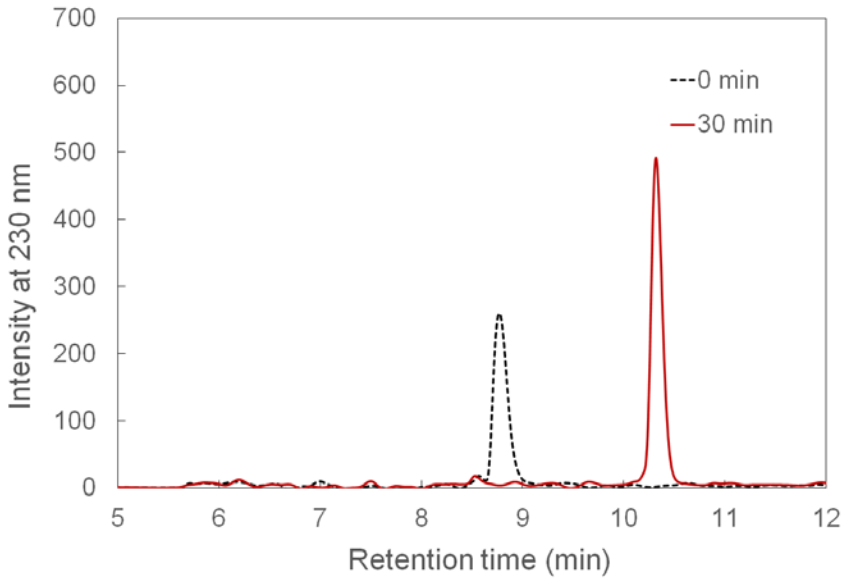

Figure S62. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3R** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

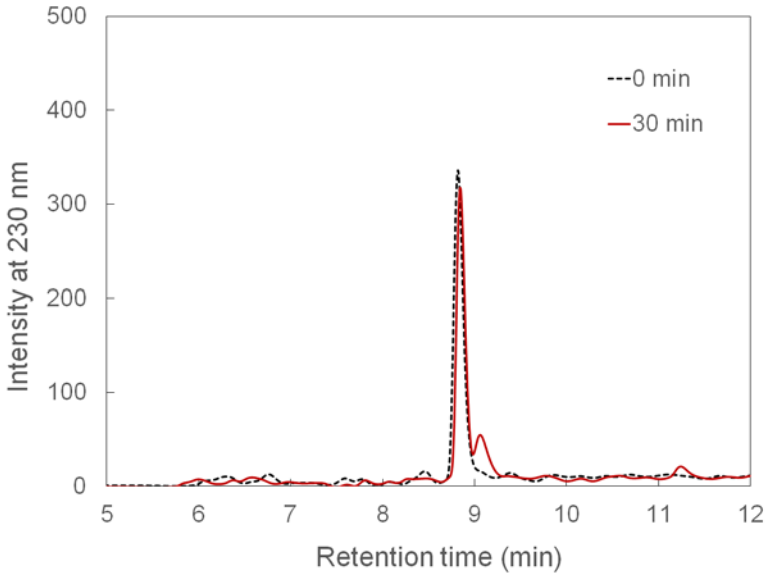

Figure S63. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3S** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

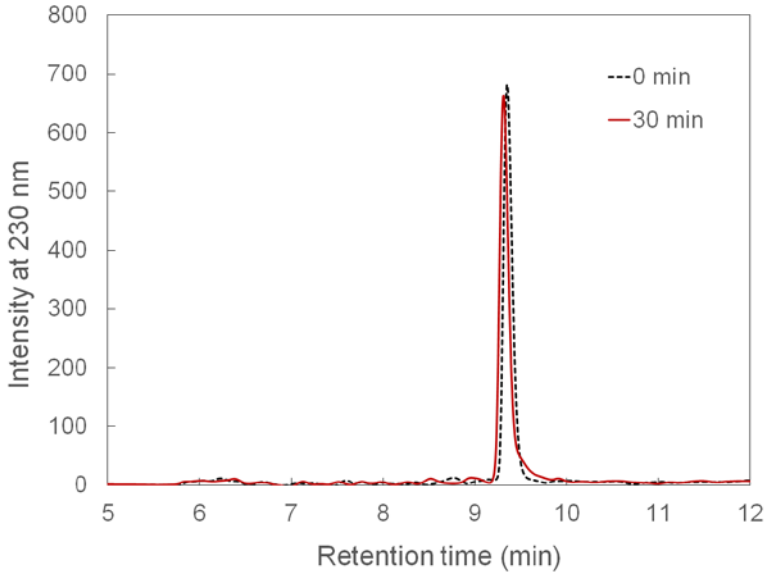

Figure S64. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3T** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

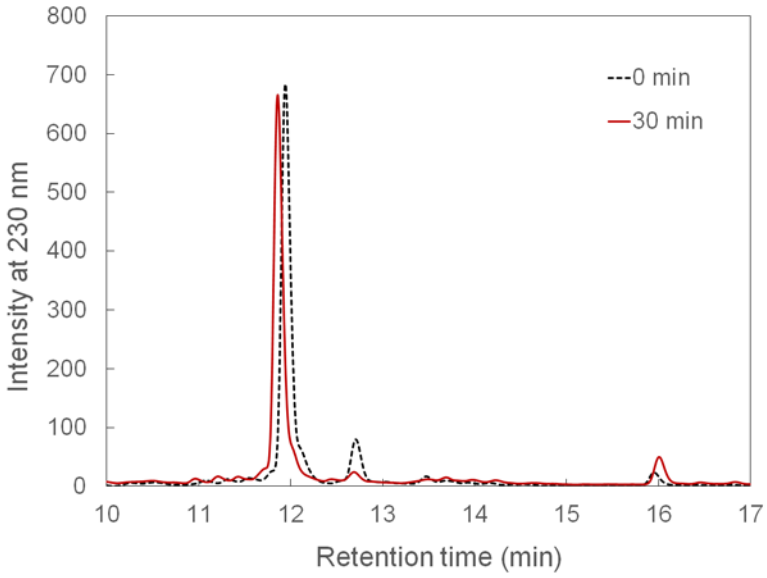

Figure S65. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3V** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

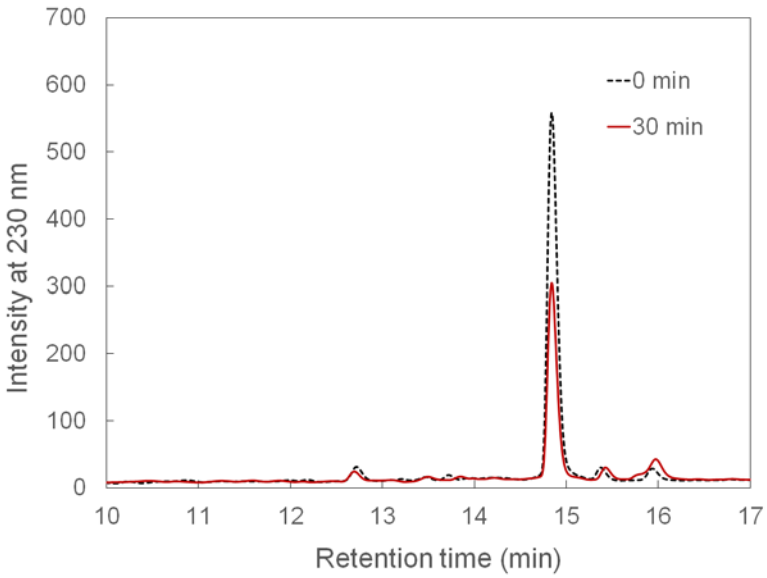

Figure S66. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3W** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

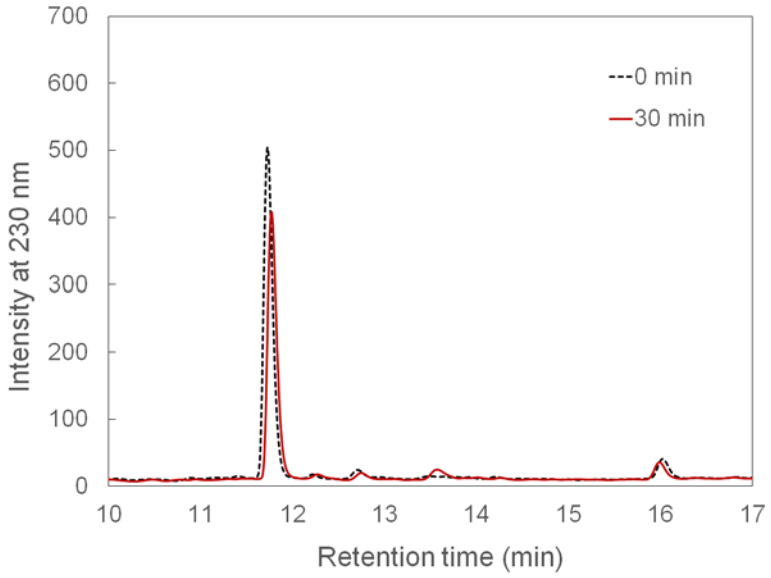

Figure S67. HPLC chromatogram of reaction mixture of **BSH** and **Cl-3Y** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

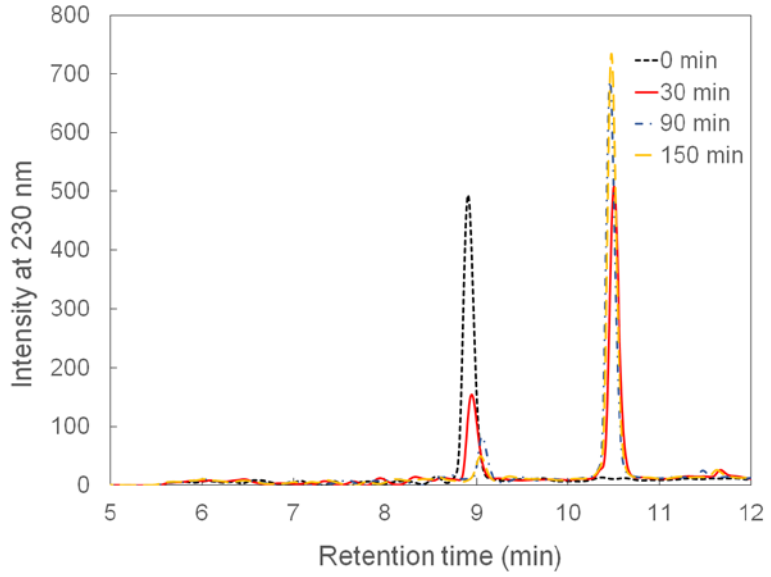

Figure S68. HPLC chromatogram of reaction mixture of **BSH** and **Cl-2R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

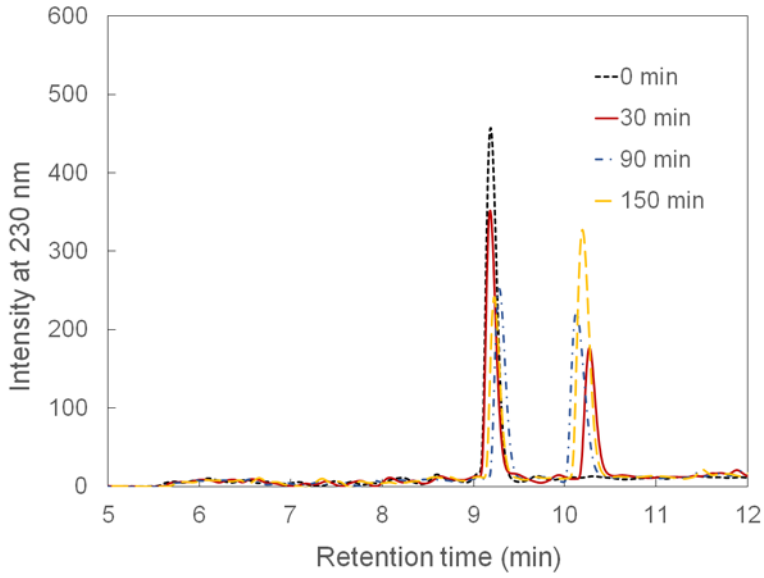

Figure S69. HPLC chromatogram of reaction mixture of **BSH** and **Cl-1R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

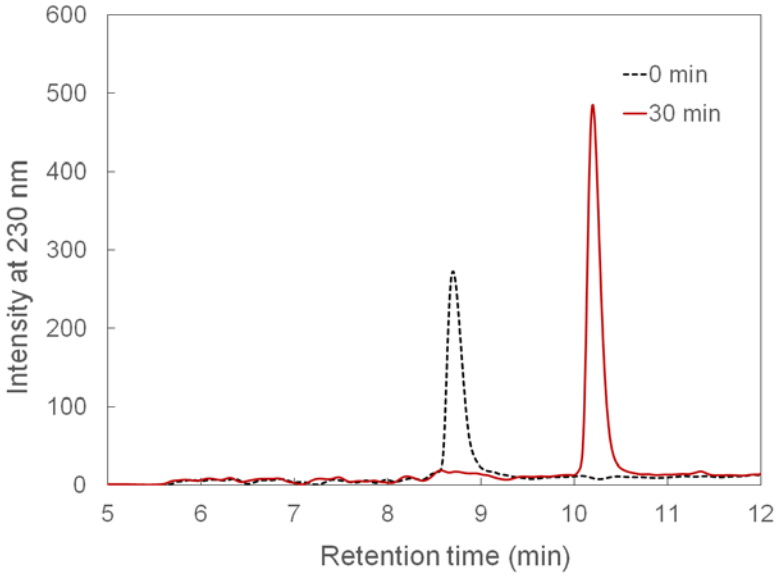

Figure S70. HPLC chromatogram of reaction mixture of **BSH** and **Cl-C1-3R** after 0 and 30 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

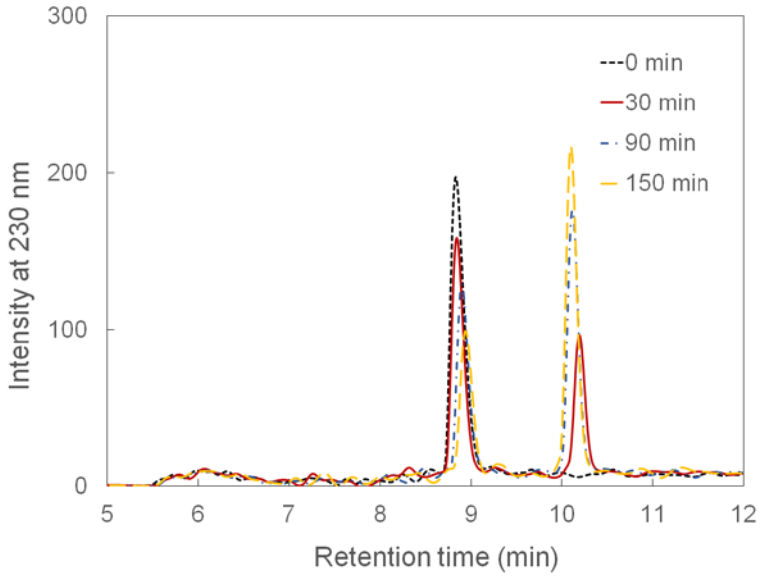

Figure S71. HPLC chromatogram of reaction mixture of **BSH** and **Cl-C2-3R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

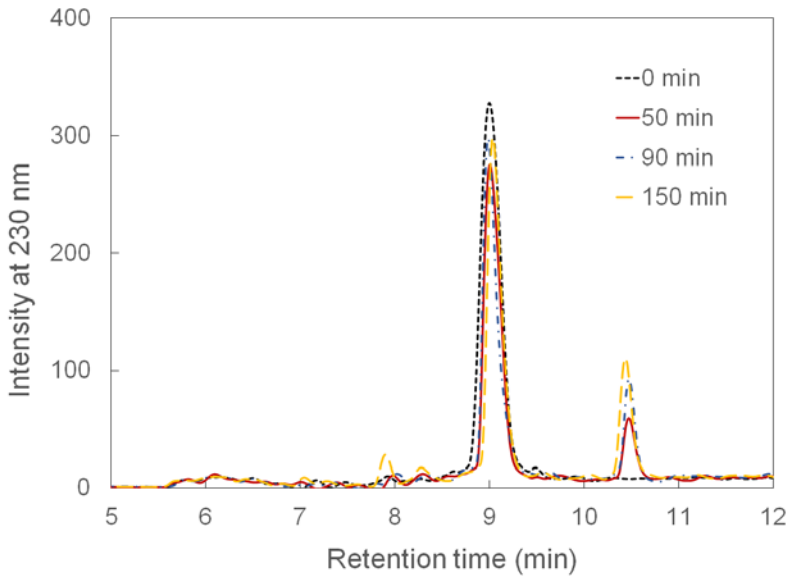

Figure S72. HPLC chromatogram of reaction mixture of **BSH** and **Cl-C4-3R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

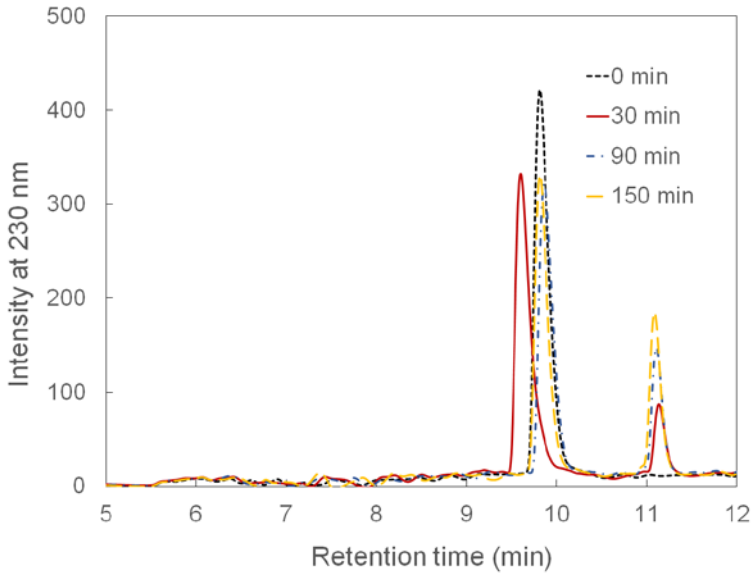

Figure S73. HPLC chromatogram of reaction mixture of **BSH** and **Cl-C7-3R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

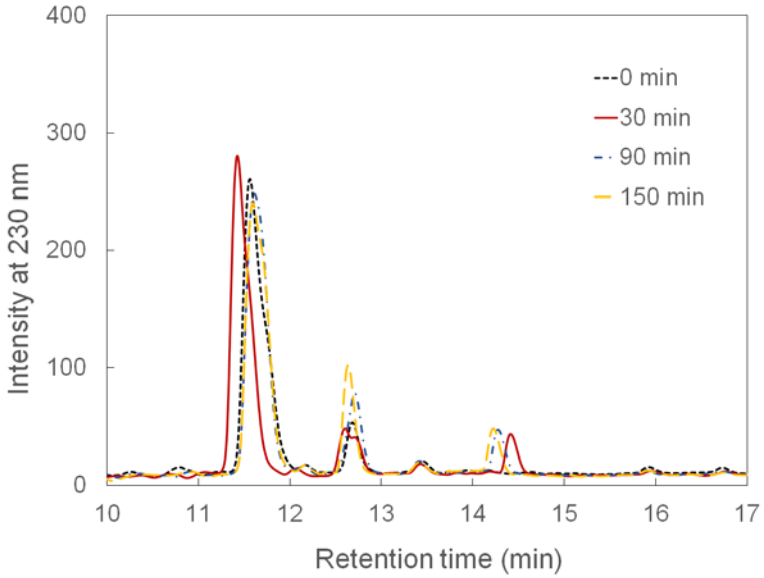

Figure S74. HPLC chromatogram of reaction mixture of **BSH** and **Cl-C11-3R** after 0, 30, 90 and 150 min. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

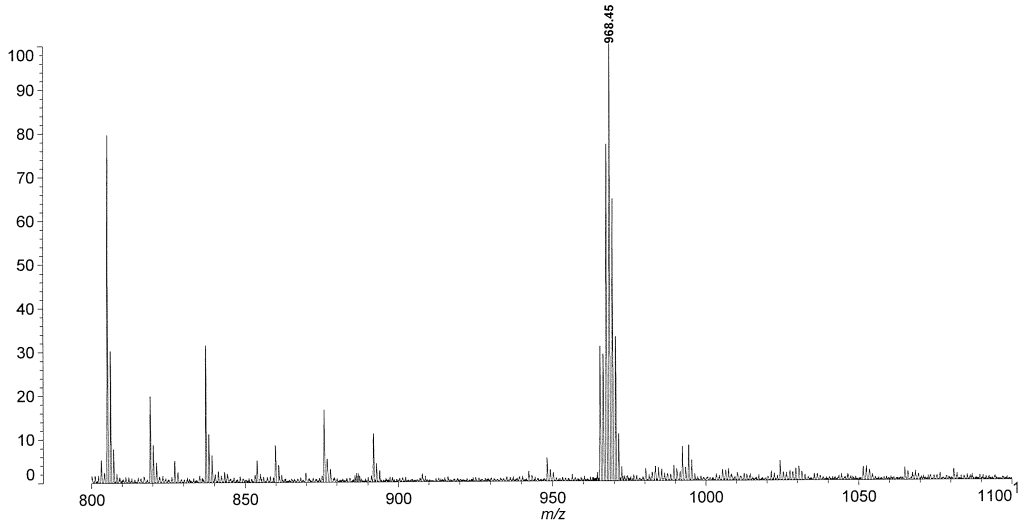

Figure S75. MALDI-TOF mass spectrum of **BS-3H**. α-CHCA was used as a matrix. **BS-3H**: calcd. $[M+H]^+$ = 968.62 and obsd. $[M+H]^+$ = 968.45.

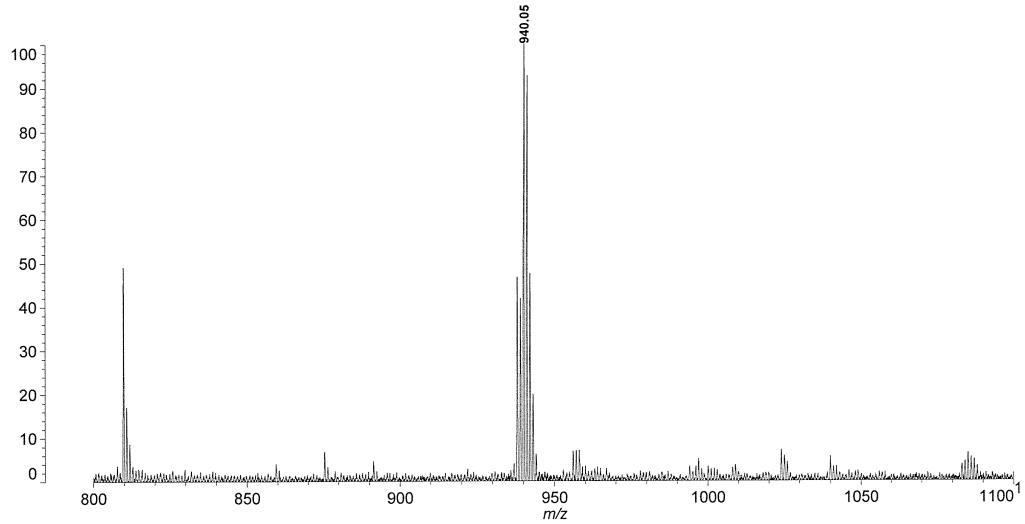

Figure S76. MALDI-TOF mass spectrum of **BS-3K**. α-CHCA was used as a matrix. **BS-3K**: calcd. $[M+H]^+$ = 941.73 and obsd. $[M+H]^+$ = 940.05.

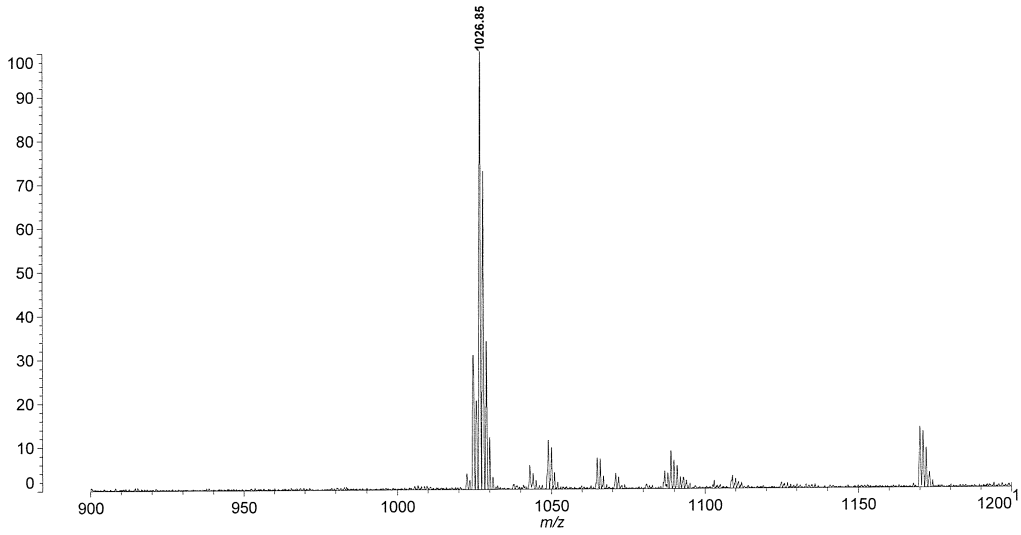

Figure S77. MALDI-TOF mass spectrum of **BS-3R**. α-CHCA was used as a matrix. **BS-3R**: calcd. $[M+H]^+$ = 1026.76 and obsd. $[M+H]^+$ = 1026.85.

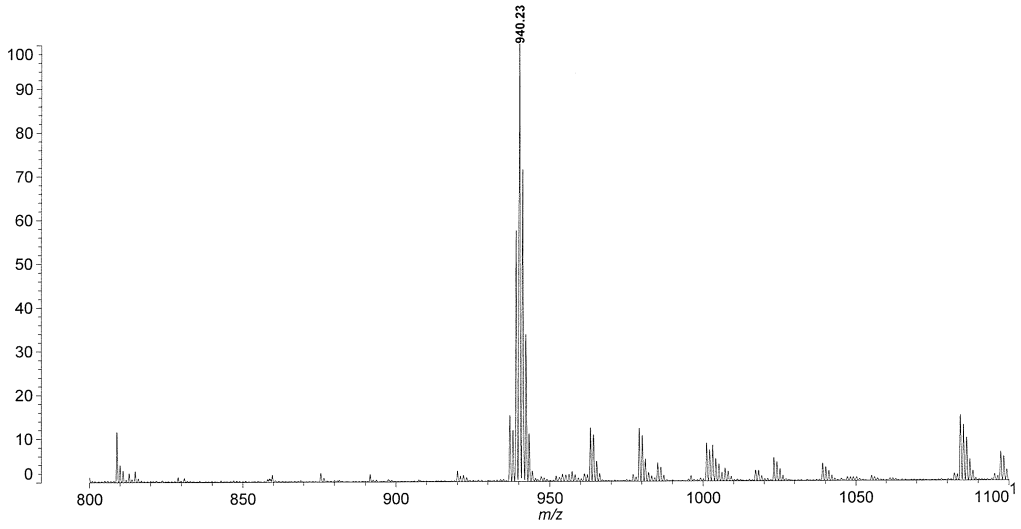

Figure S78. MALDI-TOF mass spectrum of **BS-2R**. α-CHCA was used as a matrix. **BS-2R**: calcd. $[M+H]^+$ = 940.69 and obsd. $[M+H]^+$ = 940.23.

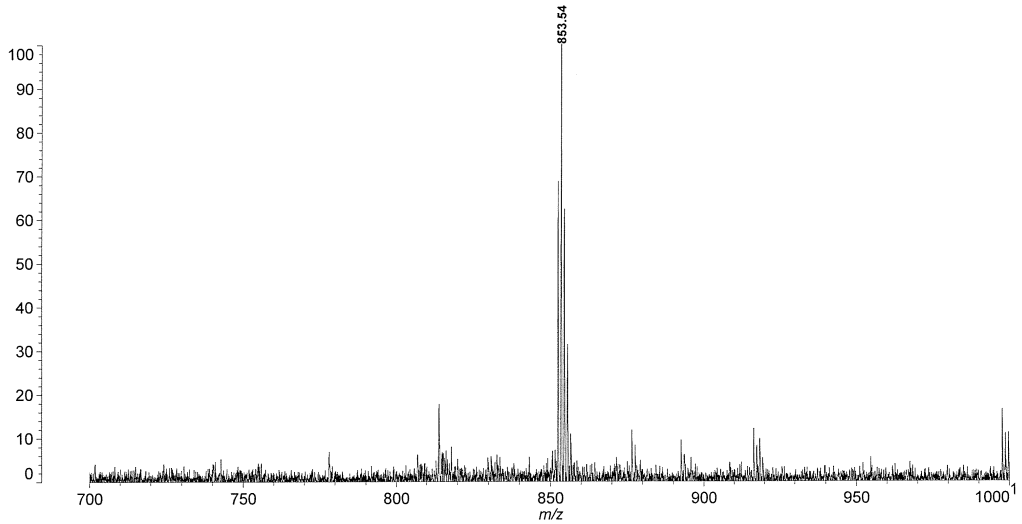

Figure S79. MALDI-TOF mass spectrum of **BS-1R**. α-CHCA was used as a matrix. **BS-1R**: calcd. $[M+H]^+$ = 855.62 and obsd. $[M+H]^+$ = 853.54. The spectrum was obtained in negative ion mode.

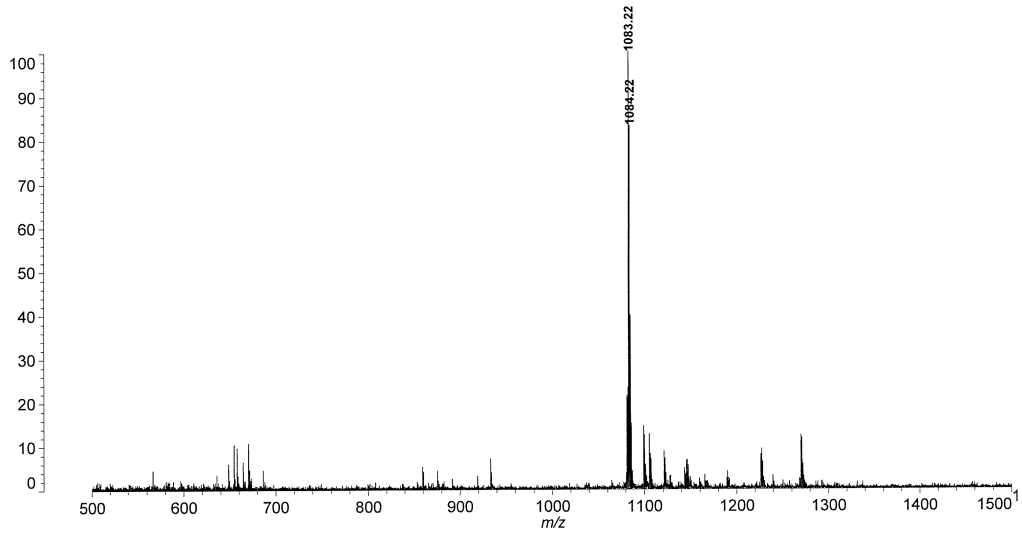

Figure S80. MALDI-TOF mass spectrum of **BS-C1-3R**. α-CHCA was used as a matrix. **BS-C1-3R**: calcd. $[M+H]^+$ = 1082.77 and obsd. $[M+H]^+$ = 1083.22.

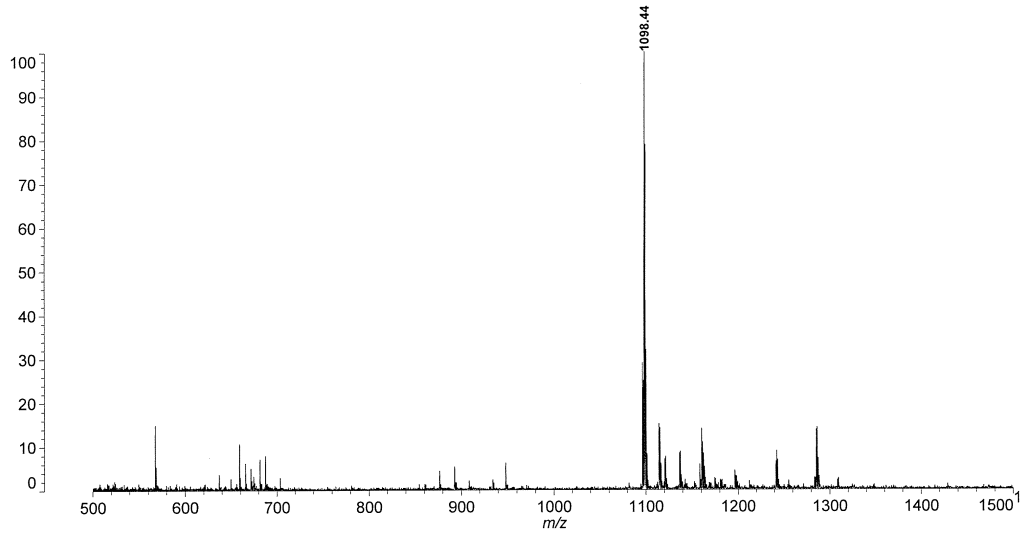

Figure S81. MALDI-TOF mass spectrum of **BS-C2-3R**. α-CHCA was used as a matrix. **BS-C2-3R**: calcd. $[M+H]^+$ = 1096.79 and obsd. $[M+H]^+$ = 1098.44.

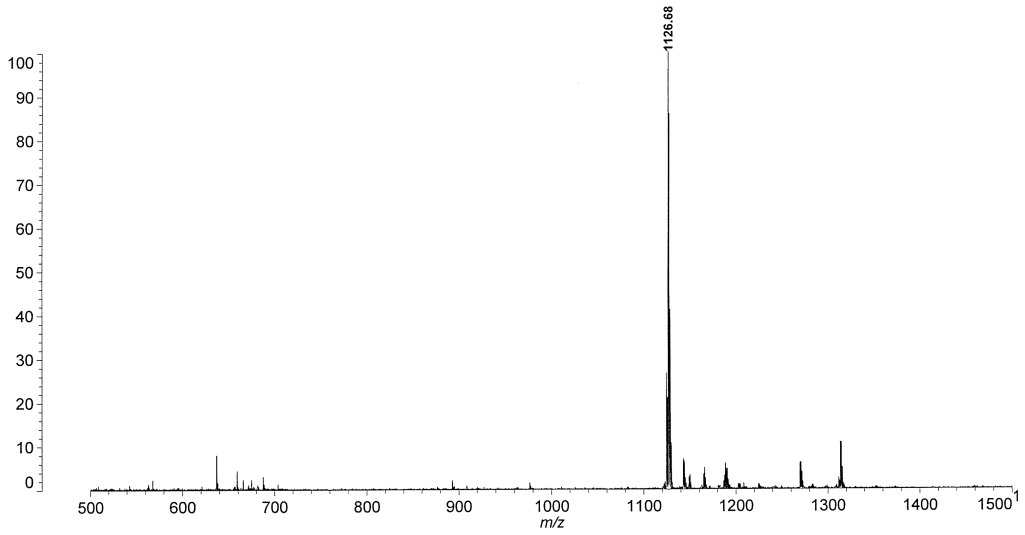

Figure S82. MALDI-TOF mass spectrum of **BS-C4-3R**. α-CHCA was used as a matrix. **BS-C4-3R**: calcd. $[M+H]^+$ = 1124.82 and obsd. $[M+H]^+$ = 1126.68.

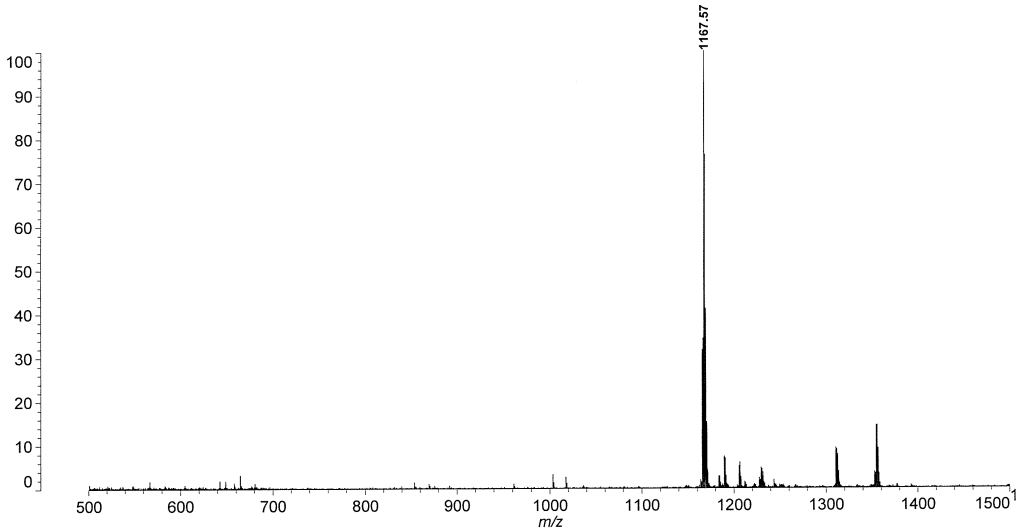

Figure S83. MALDI-TOF mass spectrum of **BS-C7-3R**. α-CHCA was used as a matrix. **BS-C7-3R**: calcd. $[M+H]^+$ = 1166.87 and obsd. $[M+H]^+$ = 1167.57.

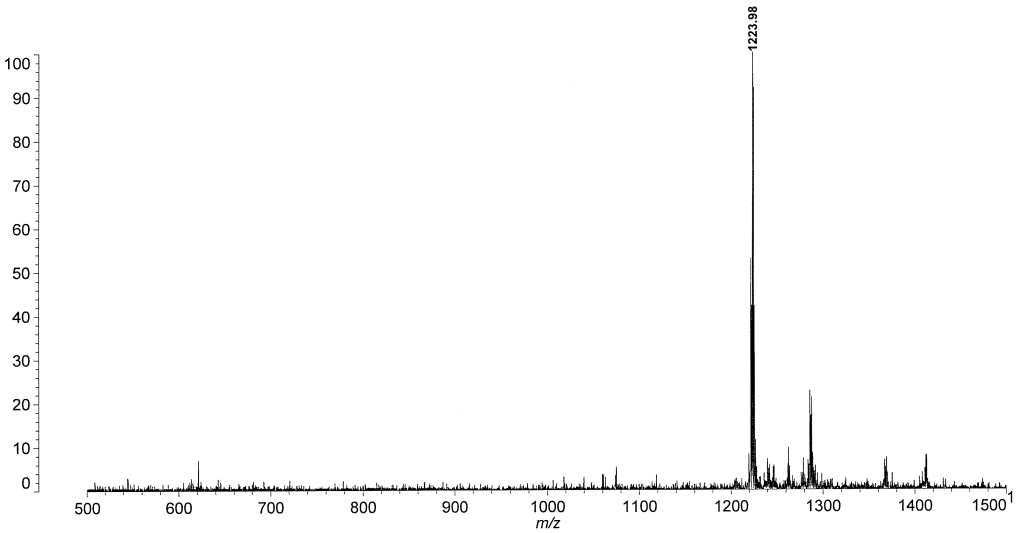

Figure S84. MALDI-TOF mass spectrum of **BS-C11-3R**. α-CHCA was used as a matrix. **BS-C11-3R**: calcd. $[M+H]^+$ = 1122.93 and obsd. $[M+H]^+$ = 1223.98.

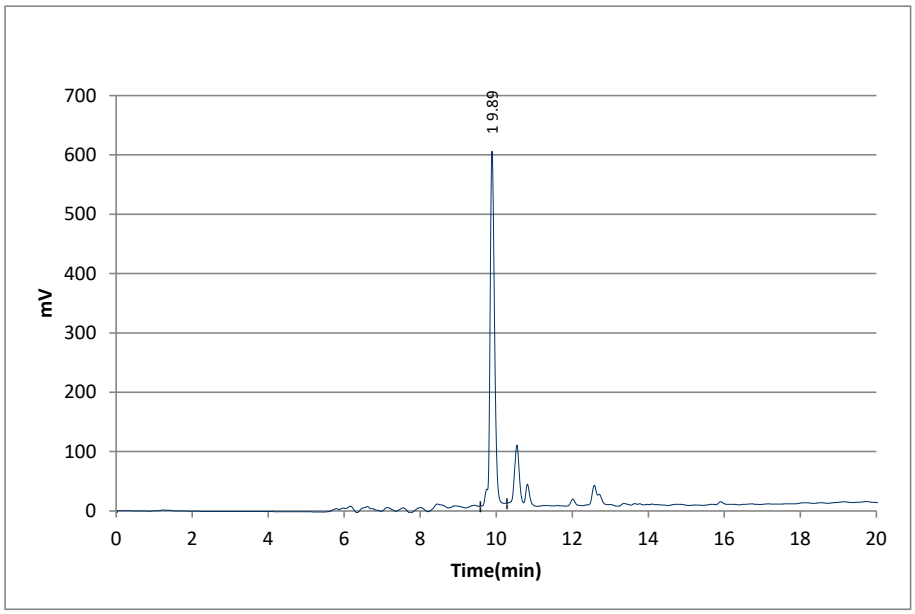

Figure S85. HPLC chromatogram of **BS-3H**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

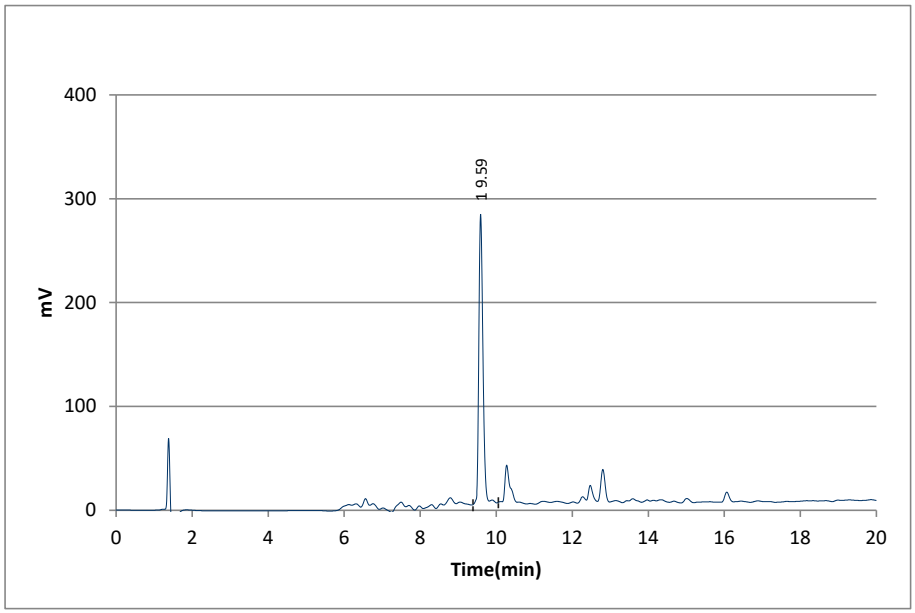

Figure S86. HPLC chromatogram of **BS-3K**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

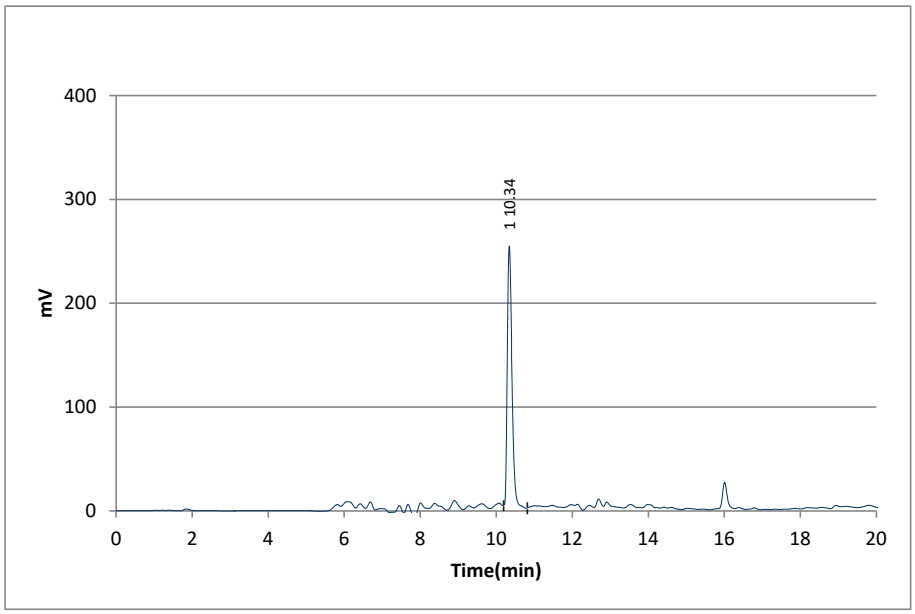

Figure S87. HPLC chromatogram of **BS-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

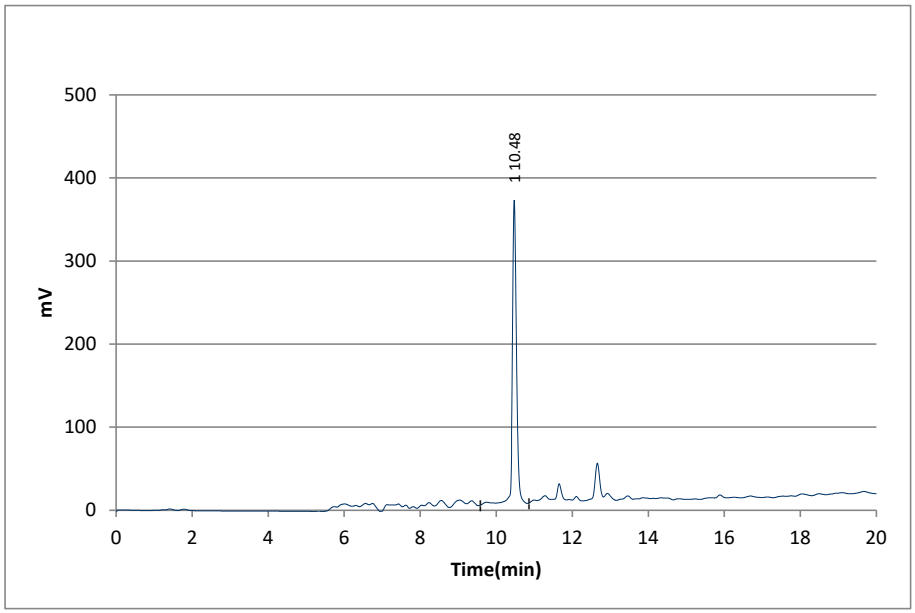

Figure S88. HPLC chromatogram of **BS-2R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

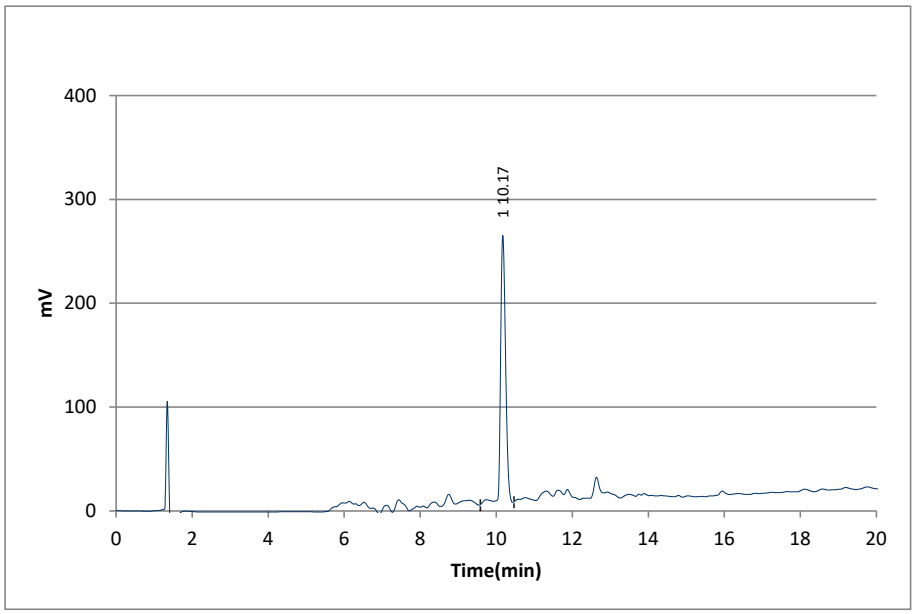

Figure S89. HPLC chromatogram of **BS-1R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

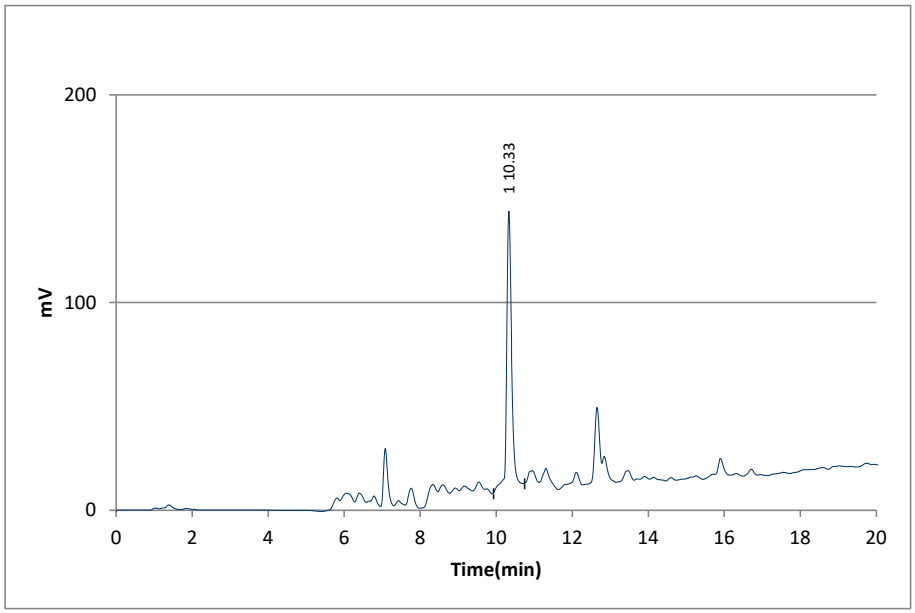

Figure S90. HPLC chromatogram of **BS-C1-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

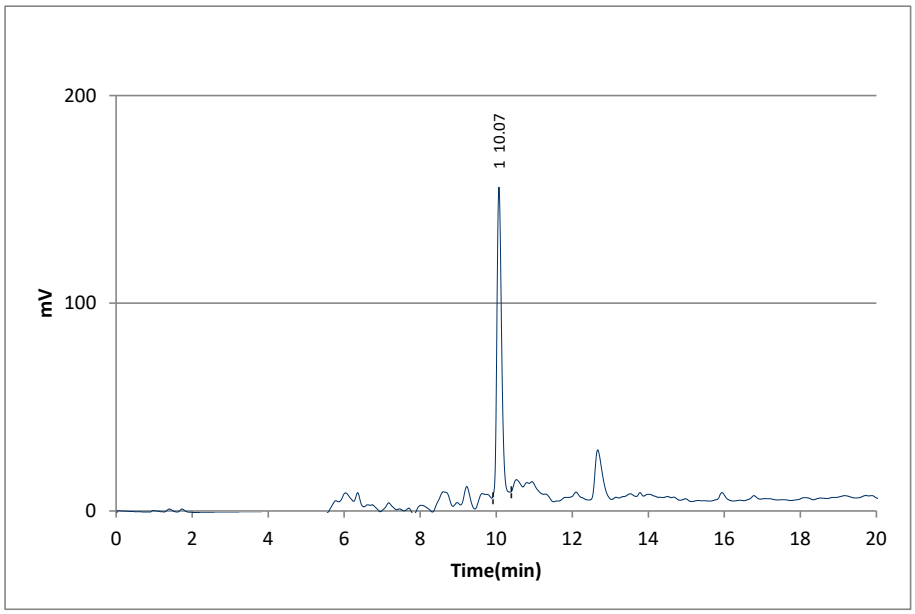

Figure S91. HPLC chromatogram of **BS-C2-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

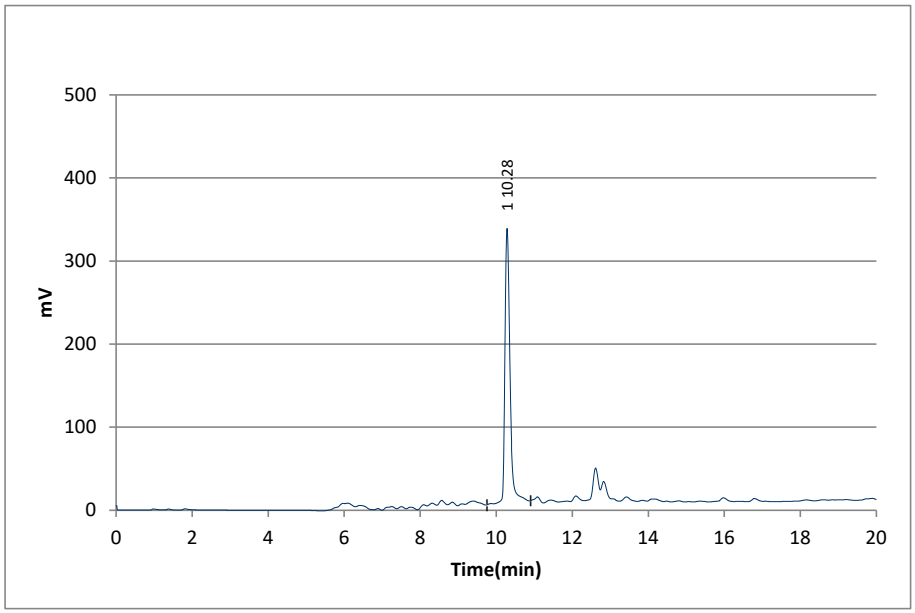

Figure S92. HPLC chromatogram of **BS-C4-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

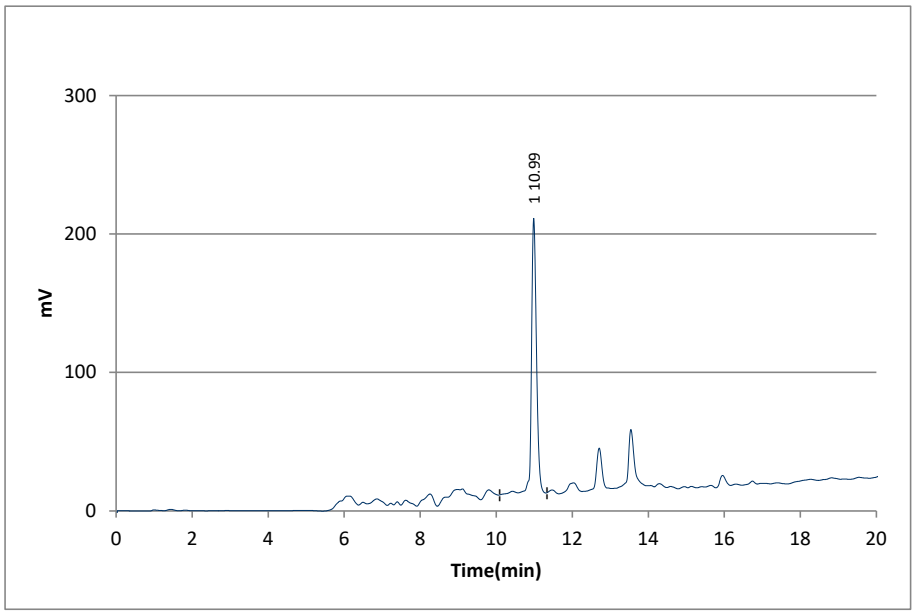

Figure S93. HPLC chromatogram of **BS-C7-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

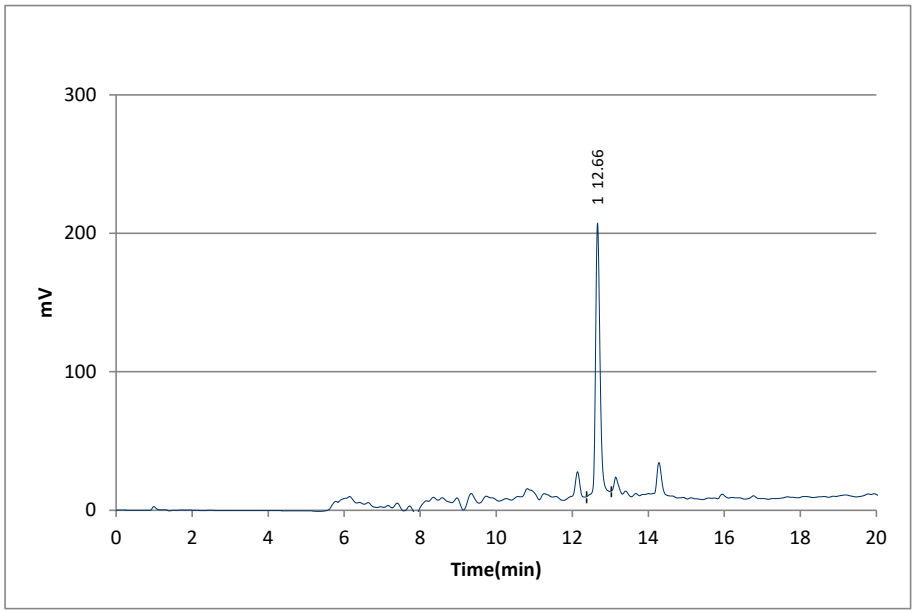

Figure S94. HPLC chromatogram of **BS-C11-3R**. The mobile phase consisted of 0.1% TFA aq. (solvent A) and acetonitrile (solvent B) at a flow rate of 1.0 mL/min and was used as a linear gradient from 0% to 100% of solvent B for 20 min. The peak was detected by measuring absorption at 230 nm.

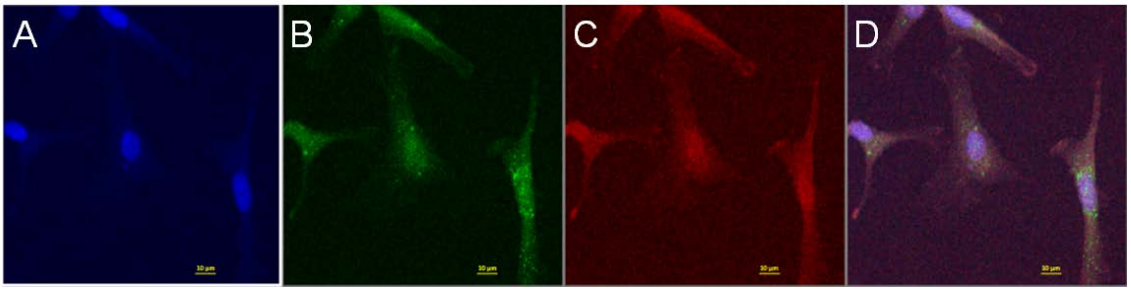

Figure S95. Typical confocal laser scanning microscope (CLSM) images of U87ΔEGFR cells after treatment with **BS-3R** for 24 h. Fluorescence signals were observed using Olympus FluoView. The final concentration of **BS-3R** was 10 μM. Panel A shows nucleus displayed as blue signals. Panel B shows BSH displayed as green signals by incubating with anti-BSH mouse mAb [6]. Panel C shows F-actin displayed as red signals. Panel D is the merging of the three images. The scale bar is 10.0 μm.