Electronic Supplementary Information

Synthesis and Characterization of a Photocleavable Collagen-Like Peptide

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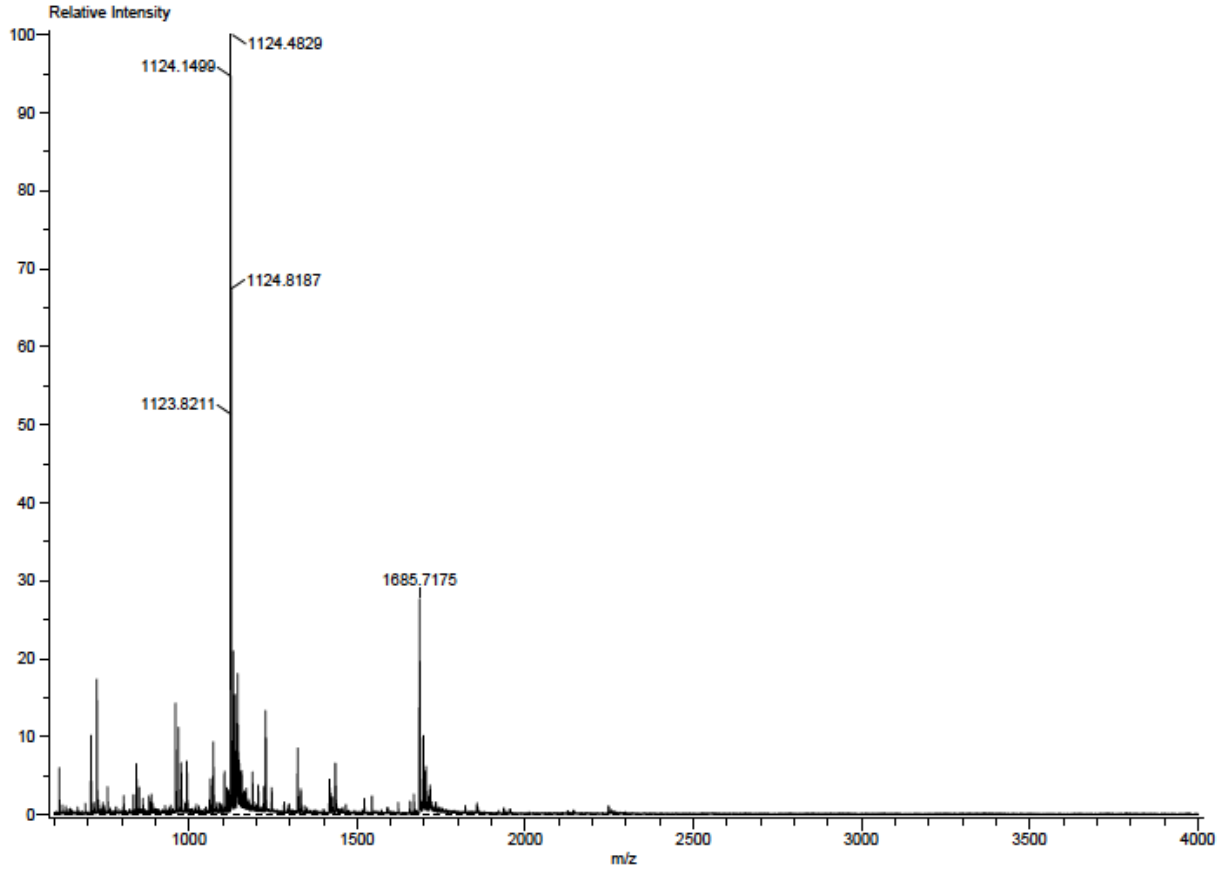
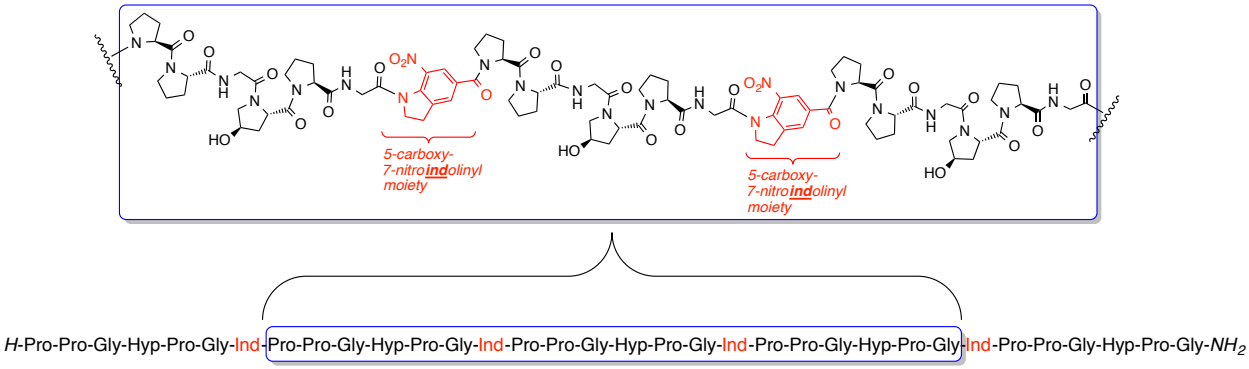
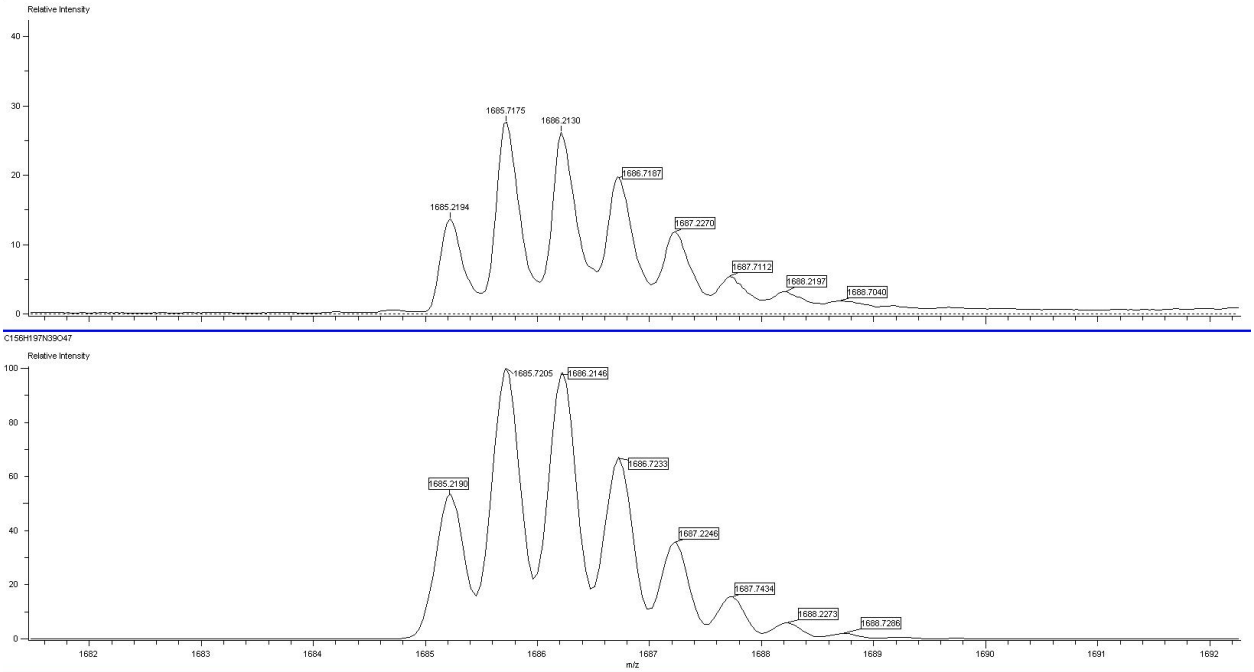


HR ESI TOF MS of peptide **1**. *m/z* $[M+2H]^{2+}$ calcd. 1685.7205 (most abundant species), obs. 1685.7175; $[M+3H]^{3+}$ calcd. 1123.8153 (monoisotopic species), obs. 1123.8211.

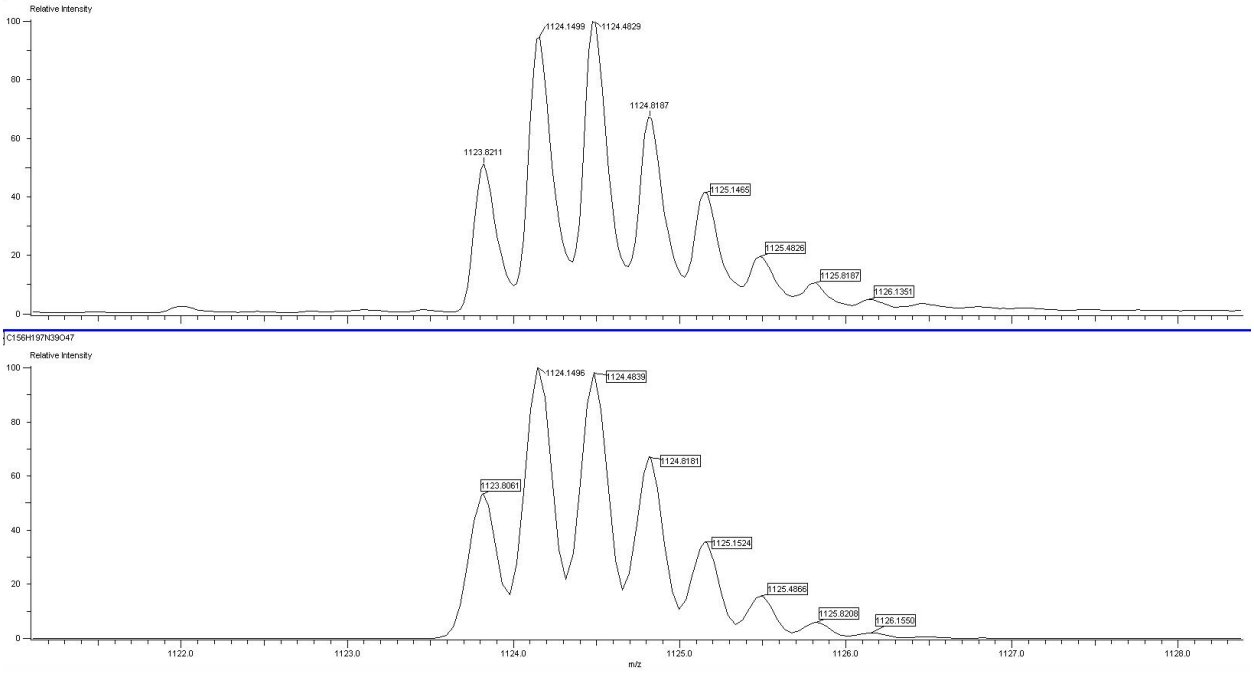


H-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-*NH*$_2$

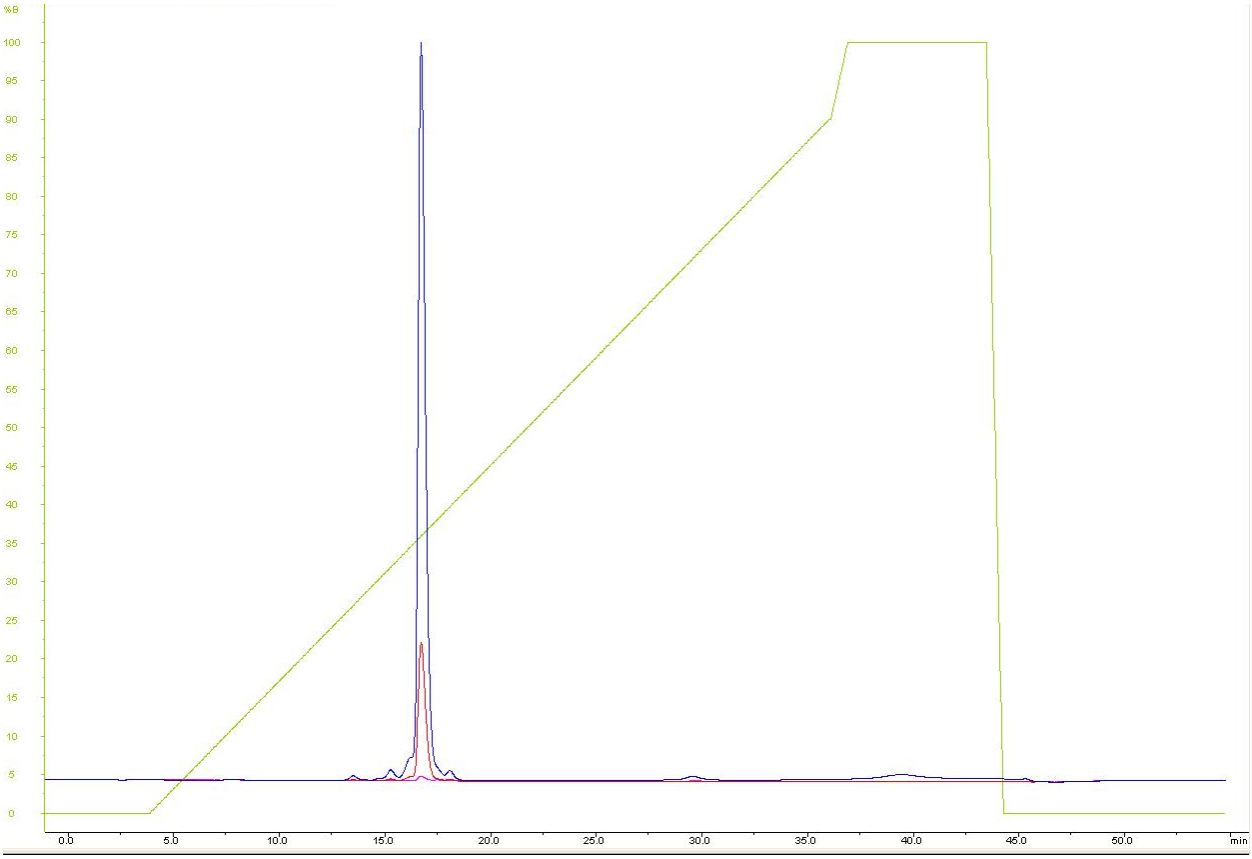
1



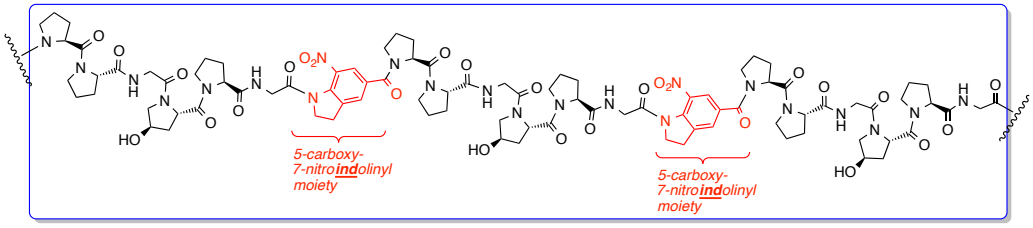
Actual (top) and simulated mass spectrum (bottom) of peptide **1** *m/z* $[M+2H]^{2+}$ (most abundant peak) calcd. 1685.7205, obs. 1685.7175.



Actual (top) and simulated mass spectrum (bottom) of peptide **1** *(m/z)* $[M+3H]^{3+}$ calcd. 1123.8061 (monoisotopic species), obs. 1123.8211.

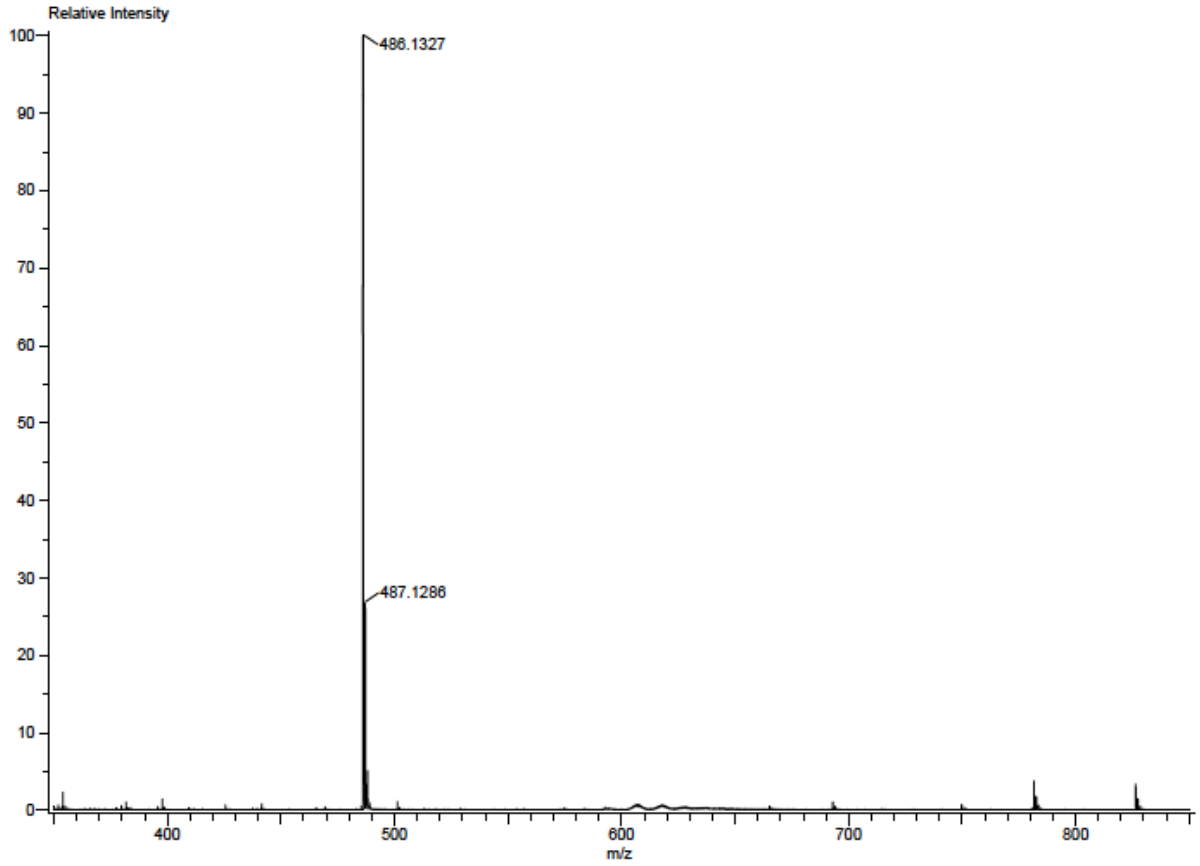


Reversed Phase FPLC profile of peptide **1**. Stationary phase: 15 μm diameter polystyrene/divinyl benzene beads; Solvent A: 2% CH_3CN and 0.1% TFA in water, solvent B: 85% CH_3CN and 0.1% TFA in water; Gradient (green): 0-90%B. Detection at 250 nm (blue), 350 nm (red), and 430 nm (pink).

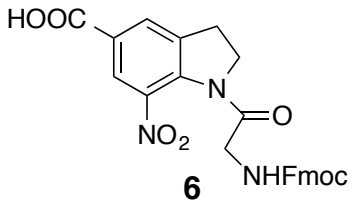


H-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-Ind-Pro-Pro-Gly-Hyp-Pro-Gly-NH_2

1



HR ESI TOF MS of amino acid building block **6**, *m/z* $[M-H]^-$ calcd. 486.1301; obs. 486.1327.



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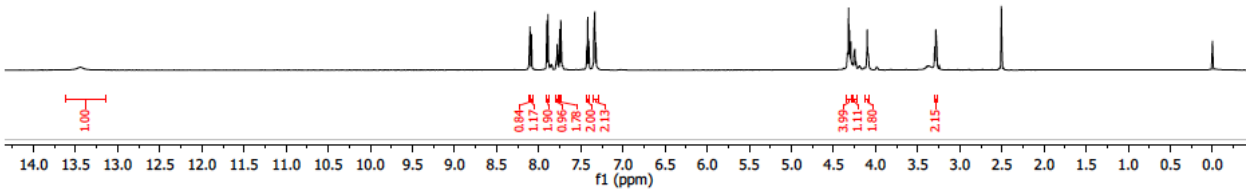
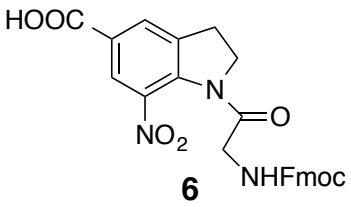


^{1}H NMR spectrum of compound **6**.



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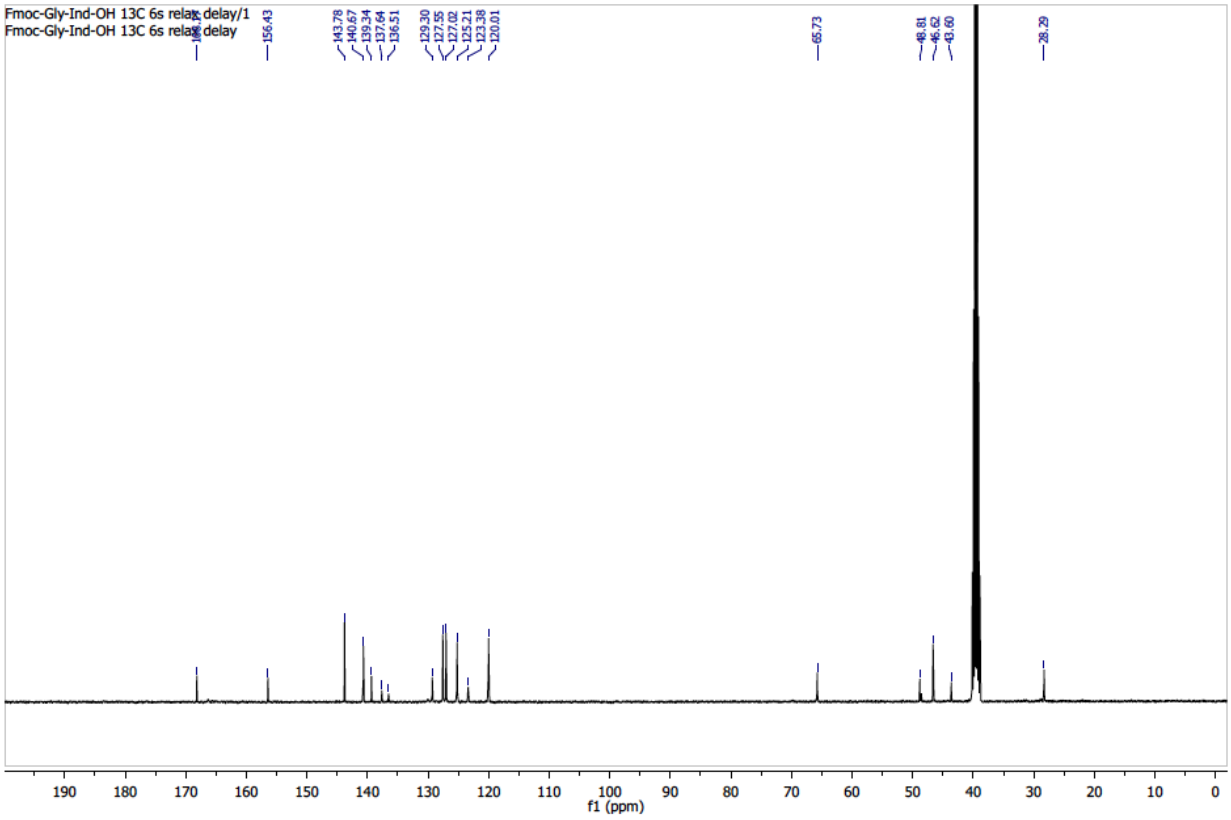
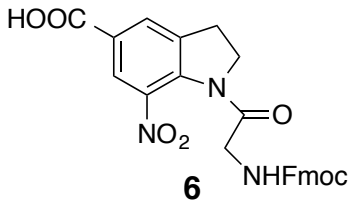


^{13}C NMR spectrum of compound **6**.



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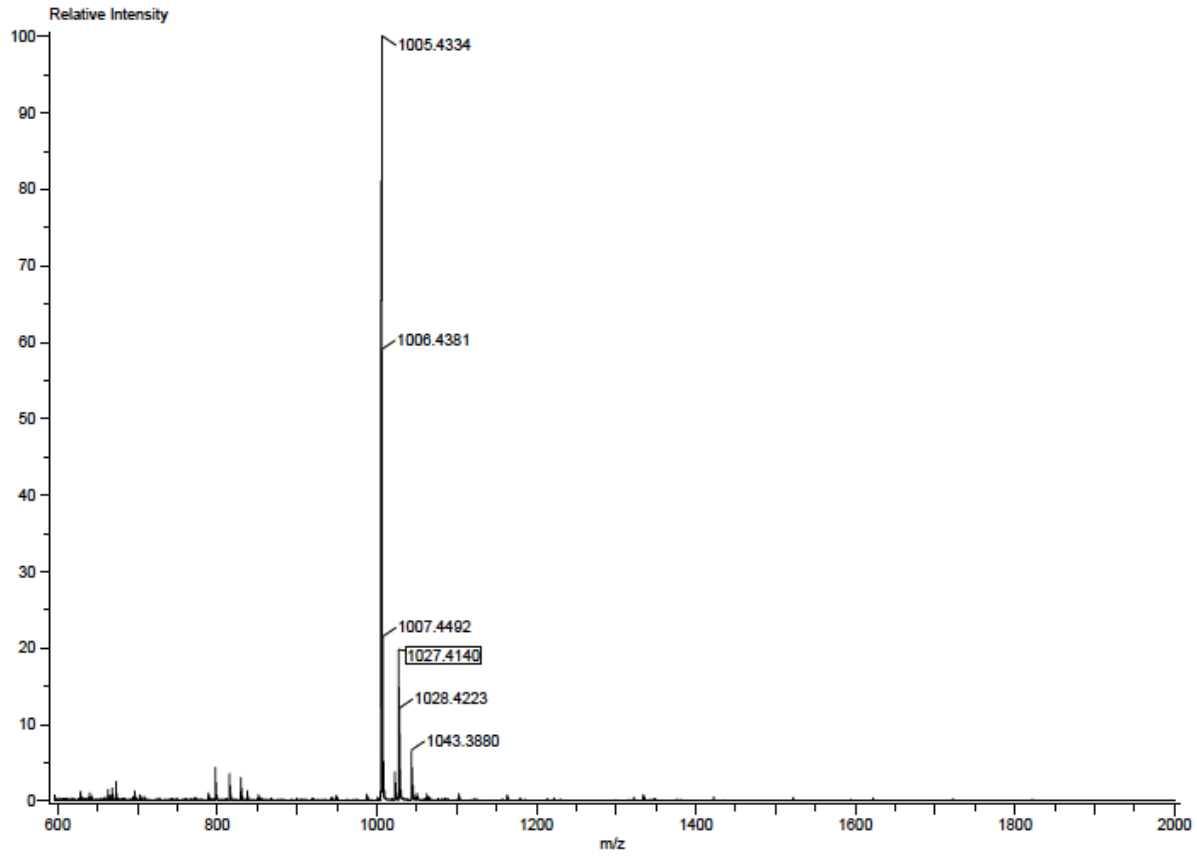
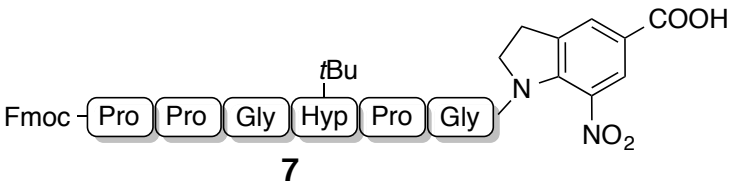
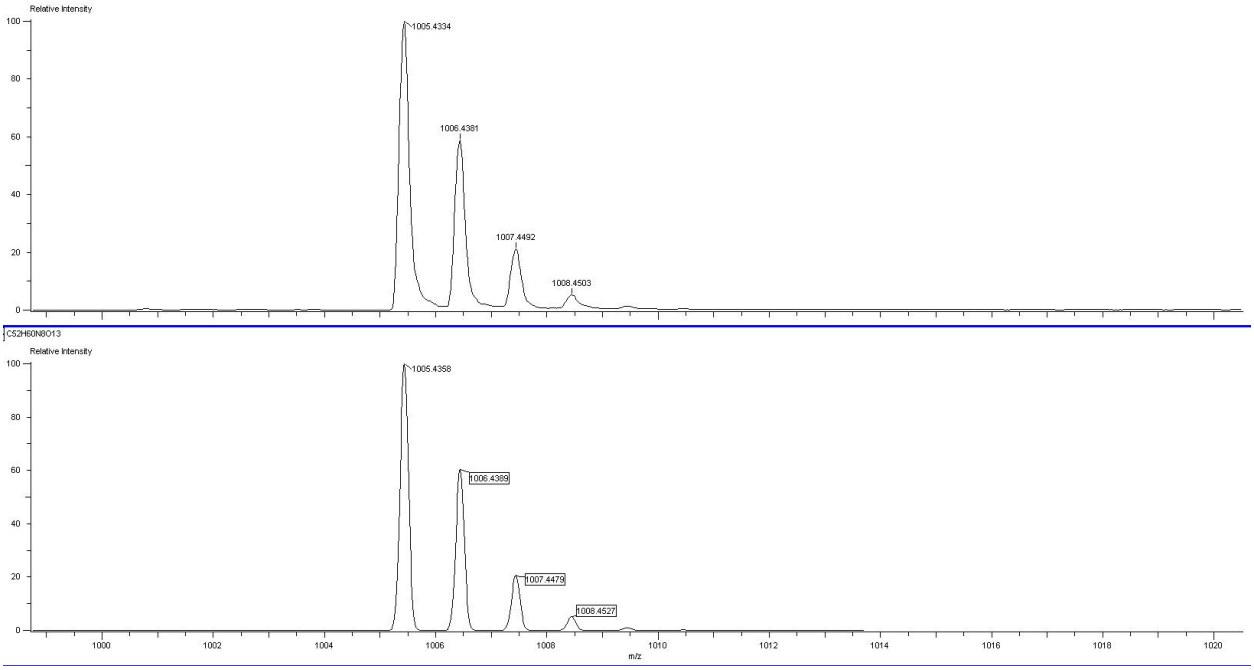


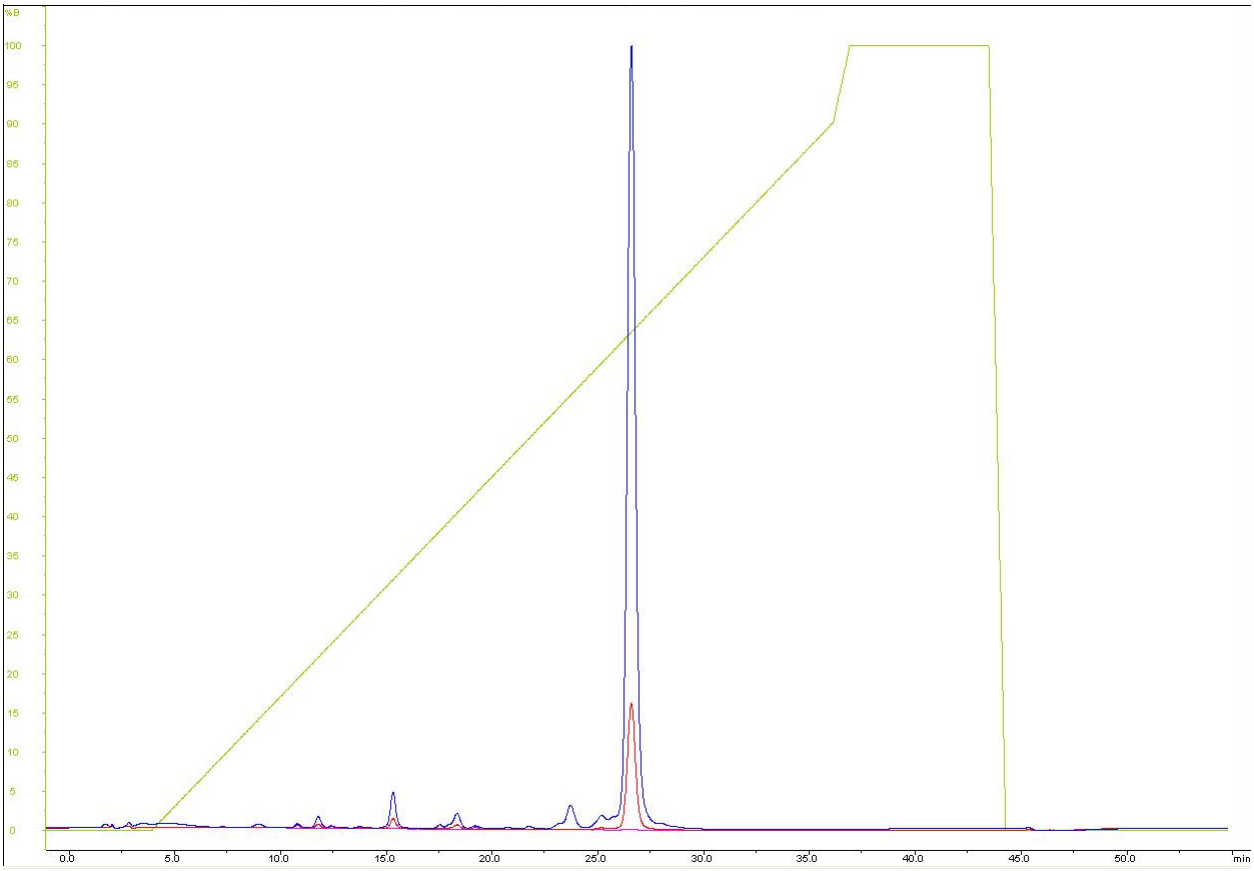
HR ESI TOF MS of peptide **7**, *m/z* $[M+H]^+$ calcd.: 1005.4358; obs. 1005.4334; $[M+Na]^+$ calcd. 1027.4178; obs. 1027.4150.



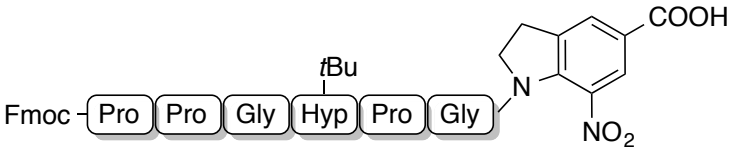
7



Actual (top) and simulated mass spectrum (bottom) of peptide **7**, *m/z* $[M+H]^+$ calcd.: 1005.4358; obs. 1005.4334.



Reversed Phase FPLC profile of peptide **7**. Stationary phase: 15 μm diameter polystyrene/divinyl benzene beads; Solvent A: 2% CH_3CN and 0.1% TFA in water, solvent B: 85% CH_3CN and 0.1% TFA in water; Gradient (green): 0-90%B. Detection at 250 nm (blue), 350 nm (red), and 430 nm (pink).



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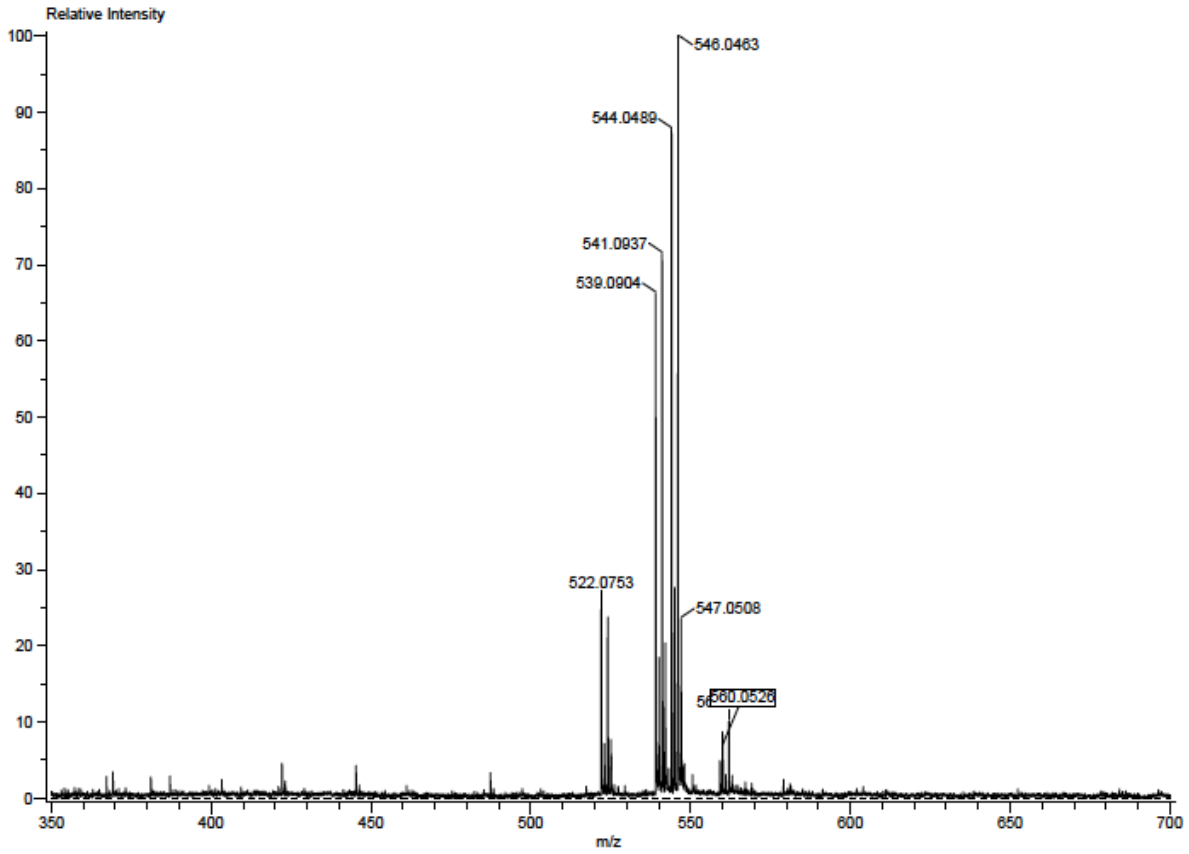
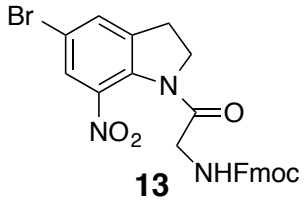


HR ESI TOF MS of compound **13**; *m/z* $[M+NH_4]^+$ calcd. 539.0930 and 541.0913, obs. 539.0904 and 541.0937; $[M+Na]^+$ calcd. 544.0484 and 546.0467, obs. 544.0489 and 546.0463.



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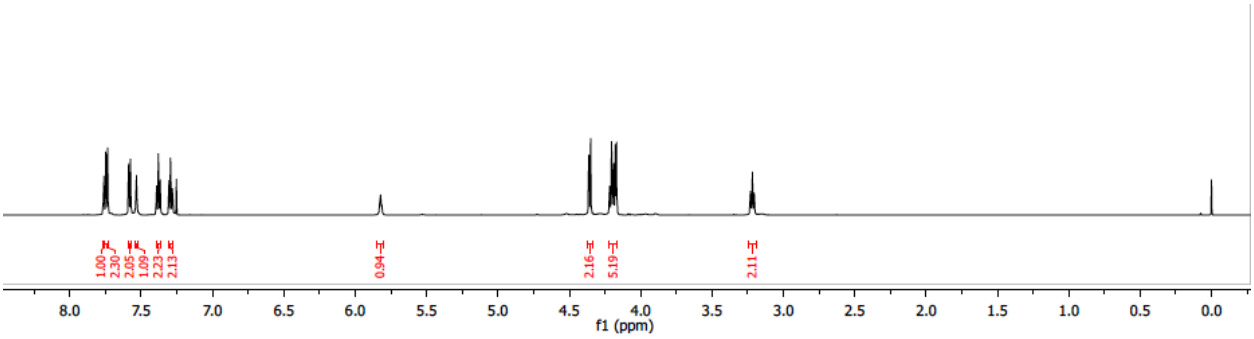
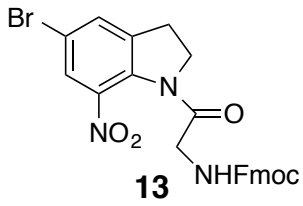


^{1}H NMR spectrum of compound **13**.



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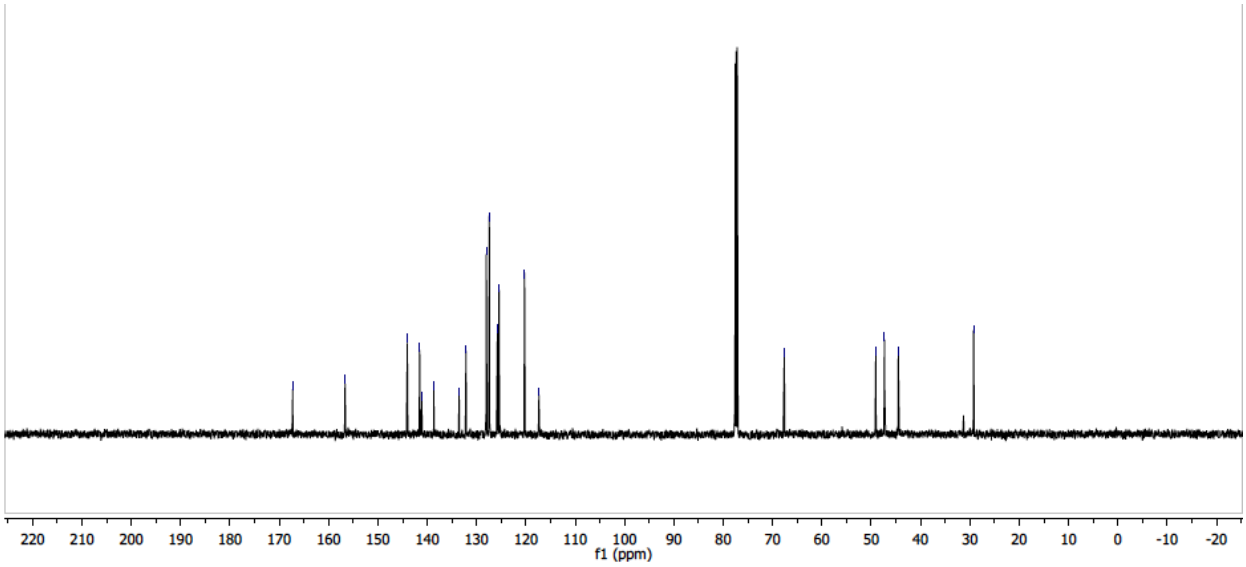
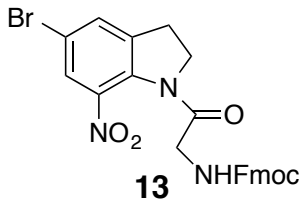


^{13}C NMR spectrum of compound **13**.



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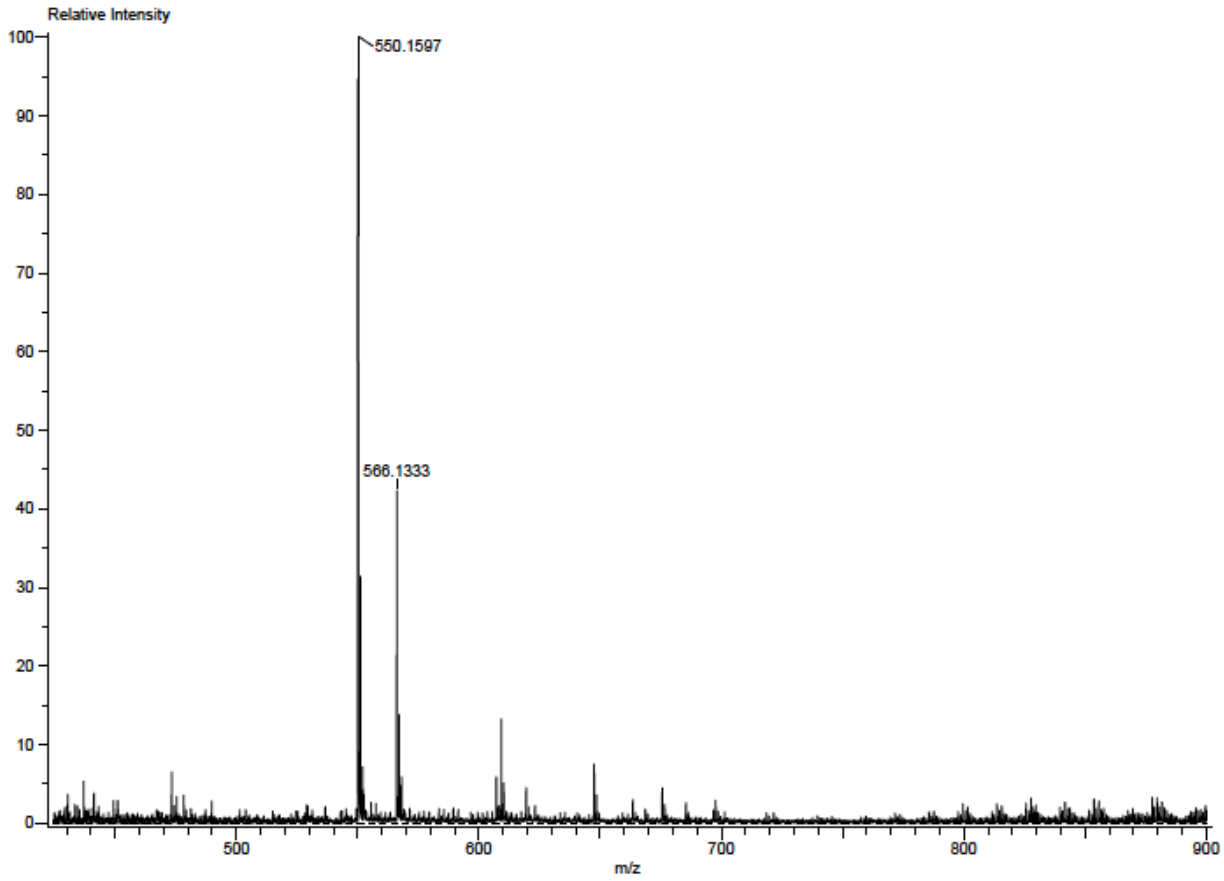
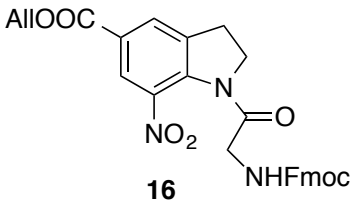
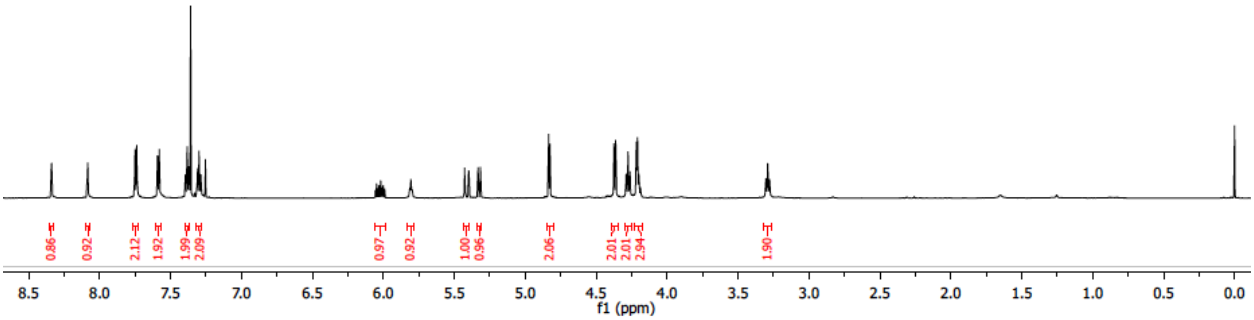


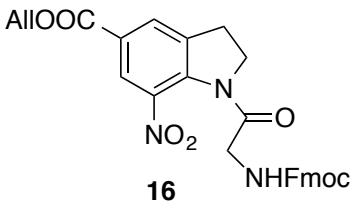
HR-ESI-TOF-MS of compound **16**; *m/z* $[M+Na]^+$ calcd. 550.1590, obs. 550.1597; $[M+K]^+$ calcd. 566.1330, obs. 566.1333.



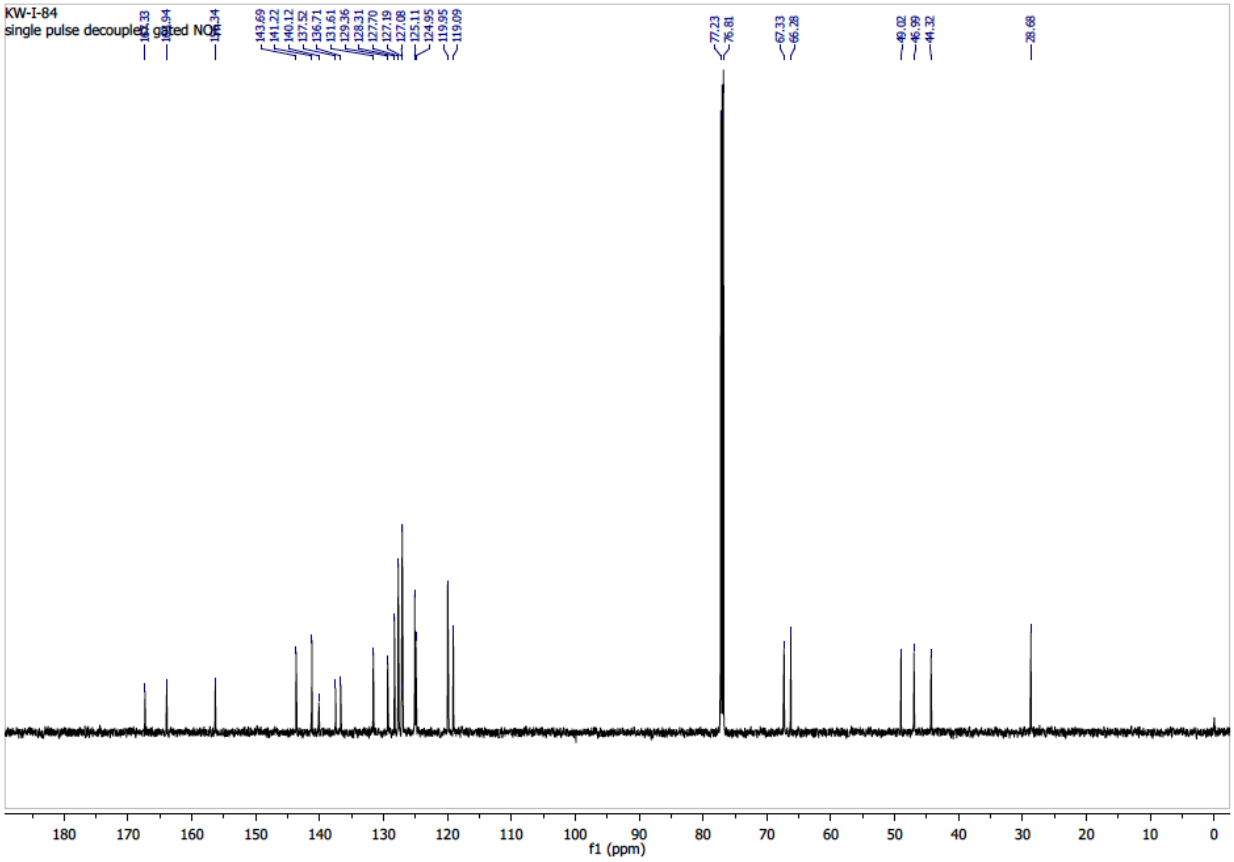
16



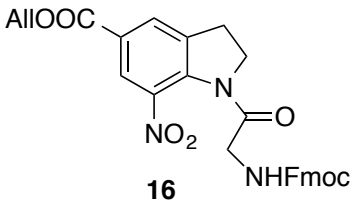
^{1}H NMR spectrum of compound **16**.



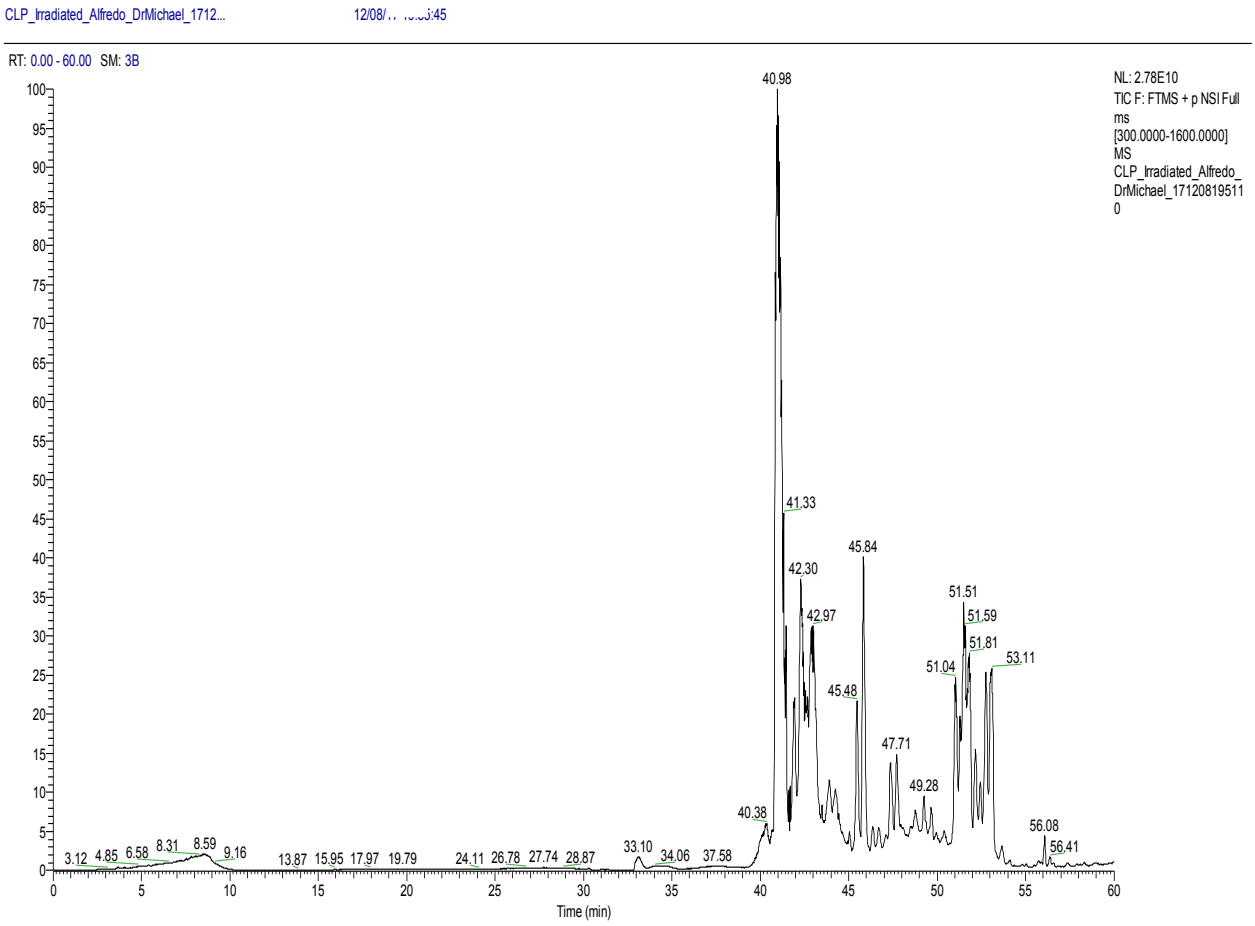
16



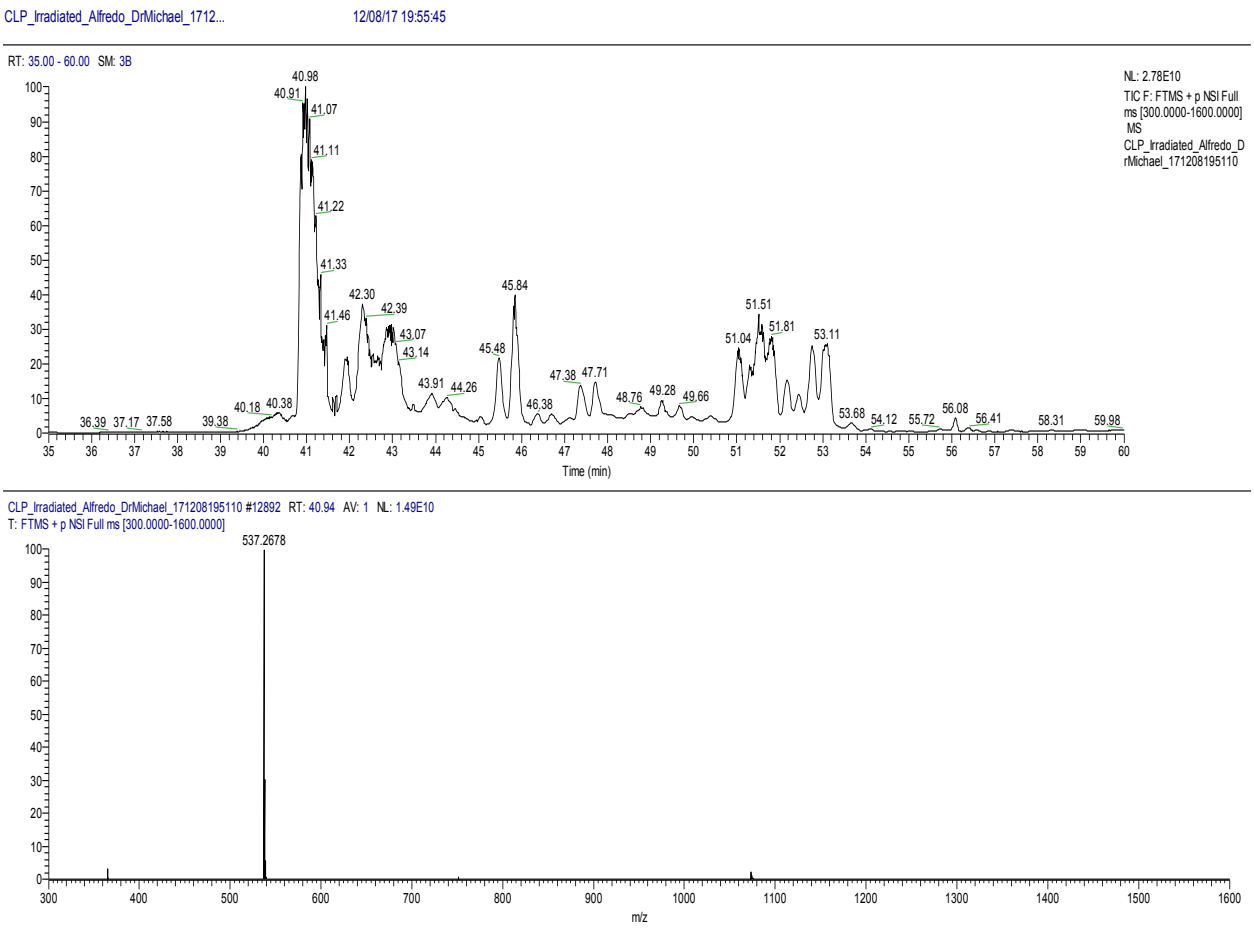
^{13}C NMR spectrum of compound **16**.



16

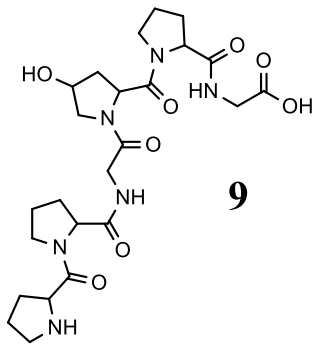


Total Ion Count (TIC)-based Nano-UHPLC chromatogram of the peptide fragments obtained after irradiation of the full length peptide **1** with 350 nm light in water.

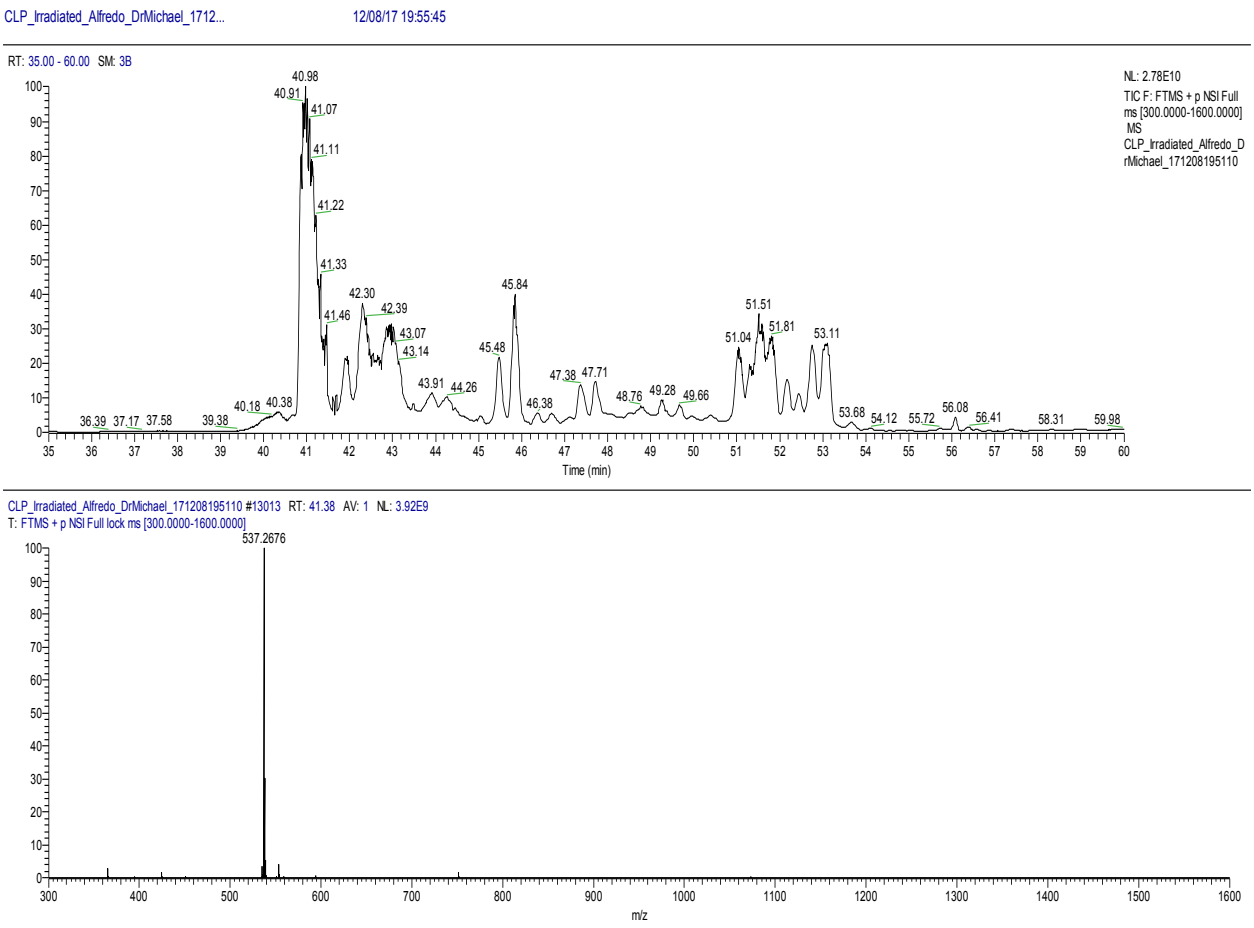


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptide **9** eluting at 40.94 min: *m/z* $[M+H]^+$ calcd. 537.2673, obs. 537.2678.

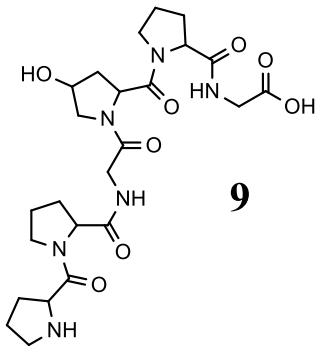


9



Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptide **9** eluting at 41.38 min: *m/z* $[M+H]^+$ calcd. 537.2673, obs. 537.2676.



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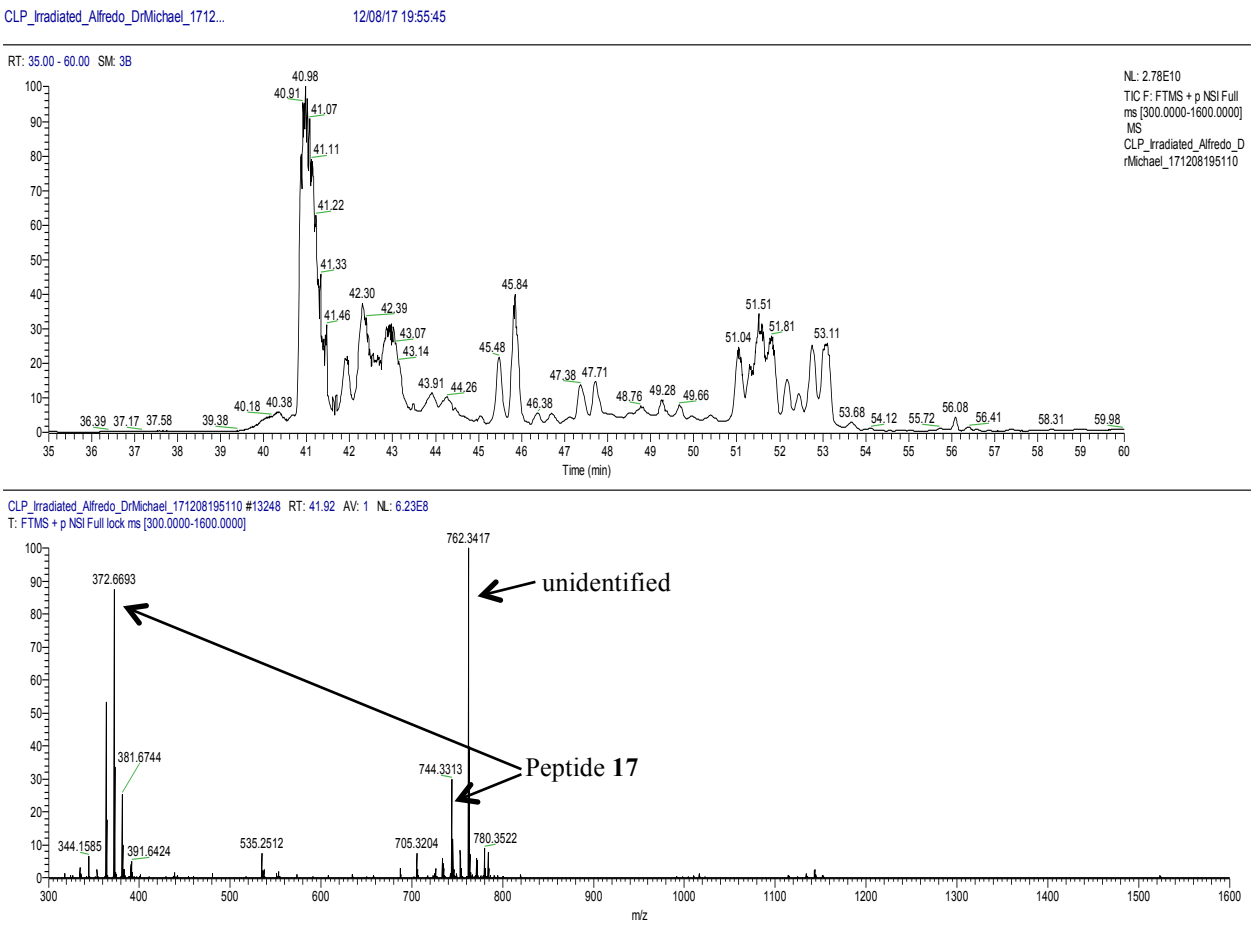
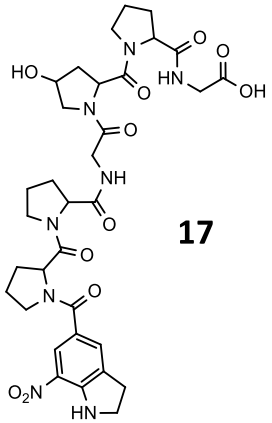
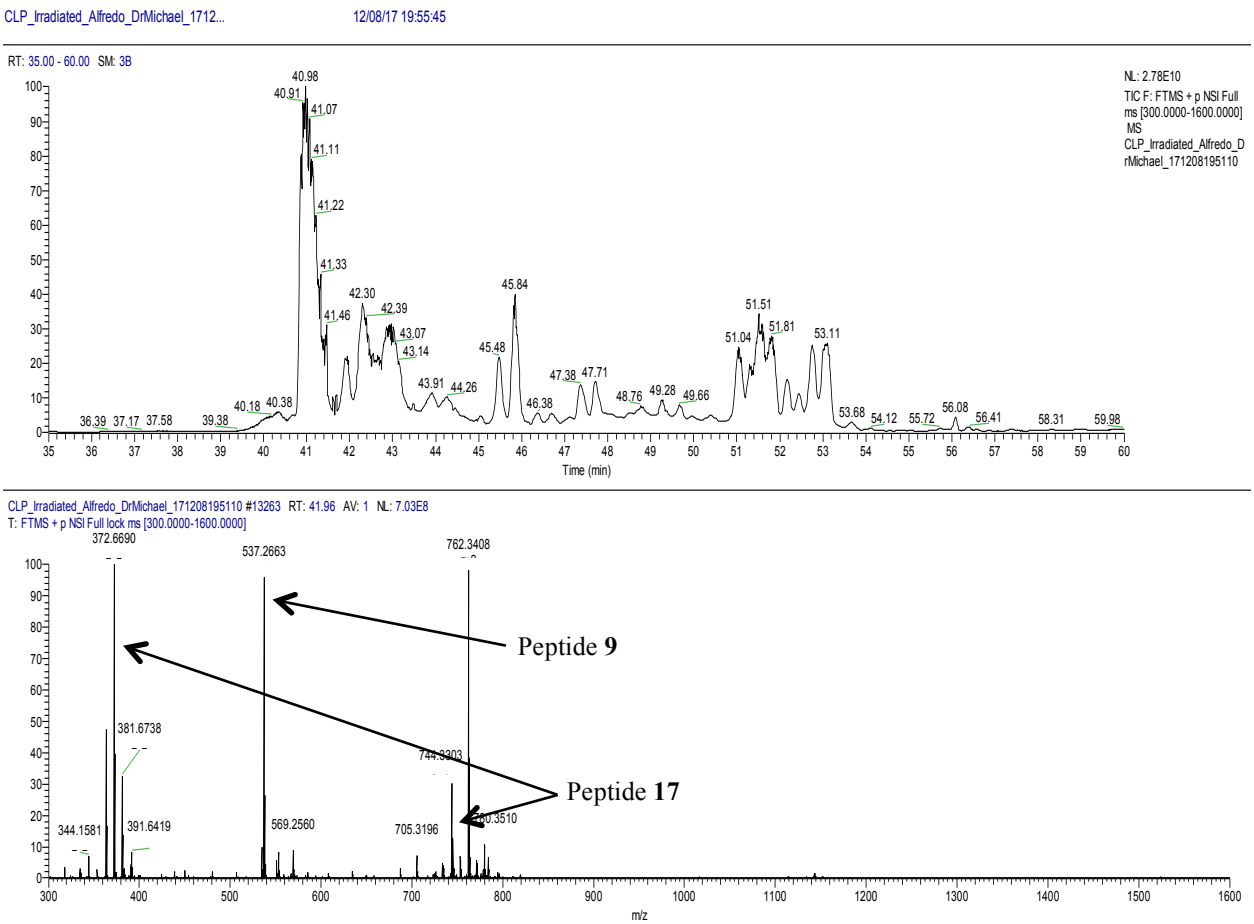


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptide **17** eluting at 41.92 min: *m/z* $[M+NH_4]^+$ calcd. 744.3317, obs. 744.3313; *m/z* $[M+H+NH_4]^{2+}$ calcd. 372.6697, obs. 372.6693.

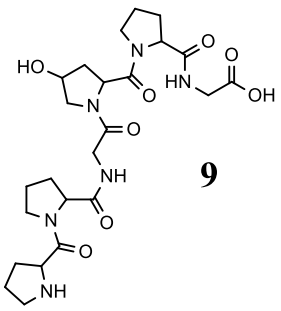


17



Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptides **9** and **17** eluting at 41.96 min: **9**, *m/z* $[M+H]^+$ calcd. 537.2673, obs. 537.2663; **17**, *m/z* $[M+NH_4]^+$ calcd. 744.3317, obs. 744.3303; *m/z* $[M+H+NH_4]^{2+}$ calcd. 372.6697, obs. 372.6690.



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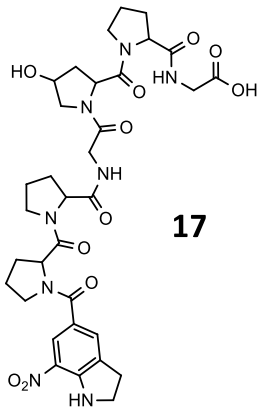
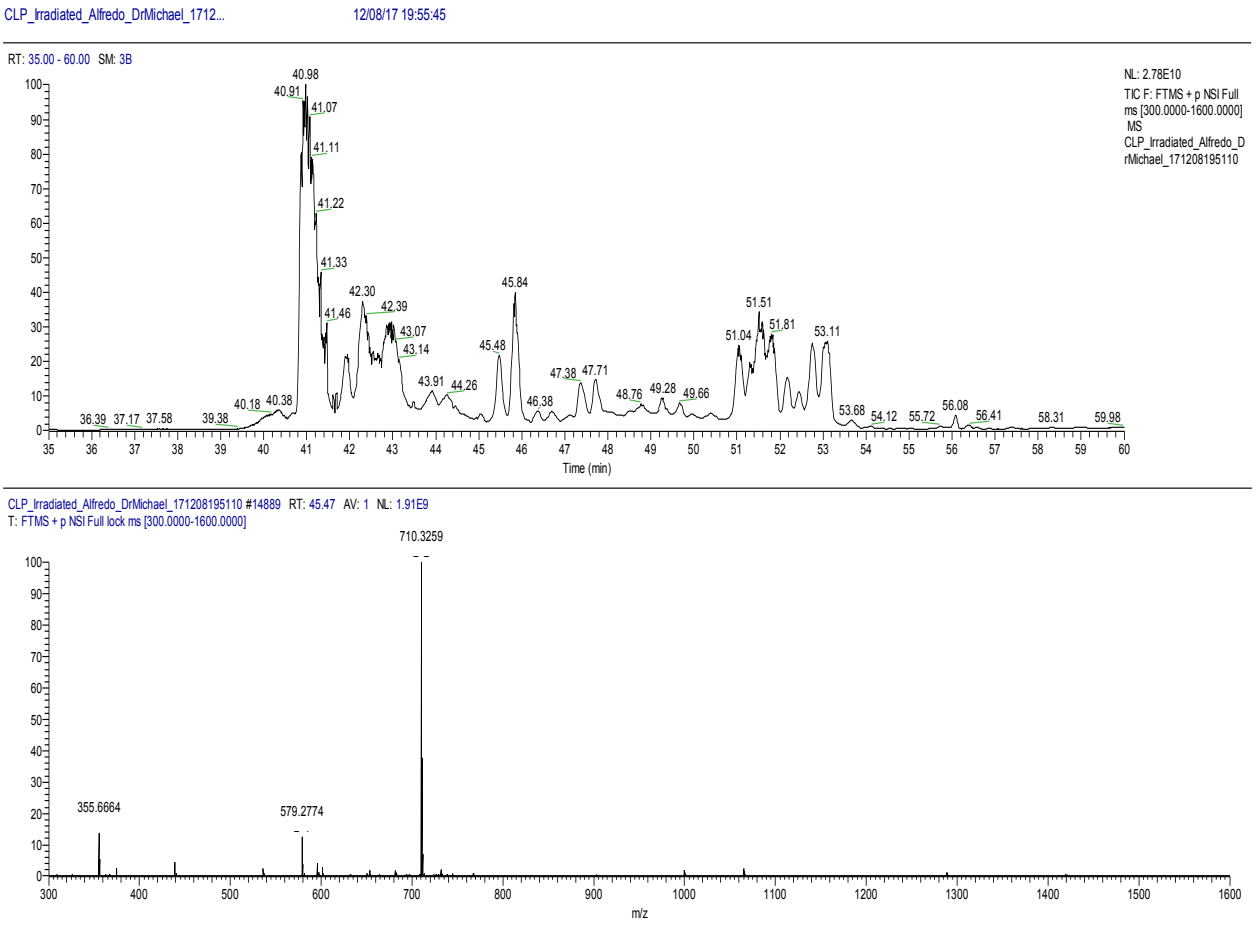
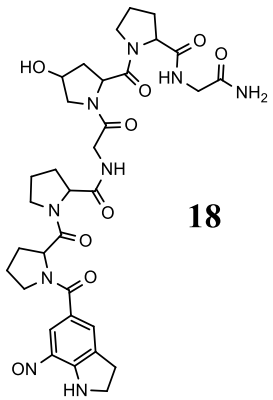


17

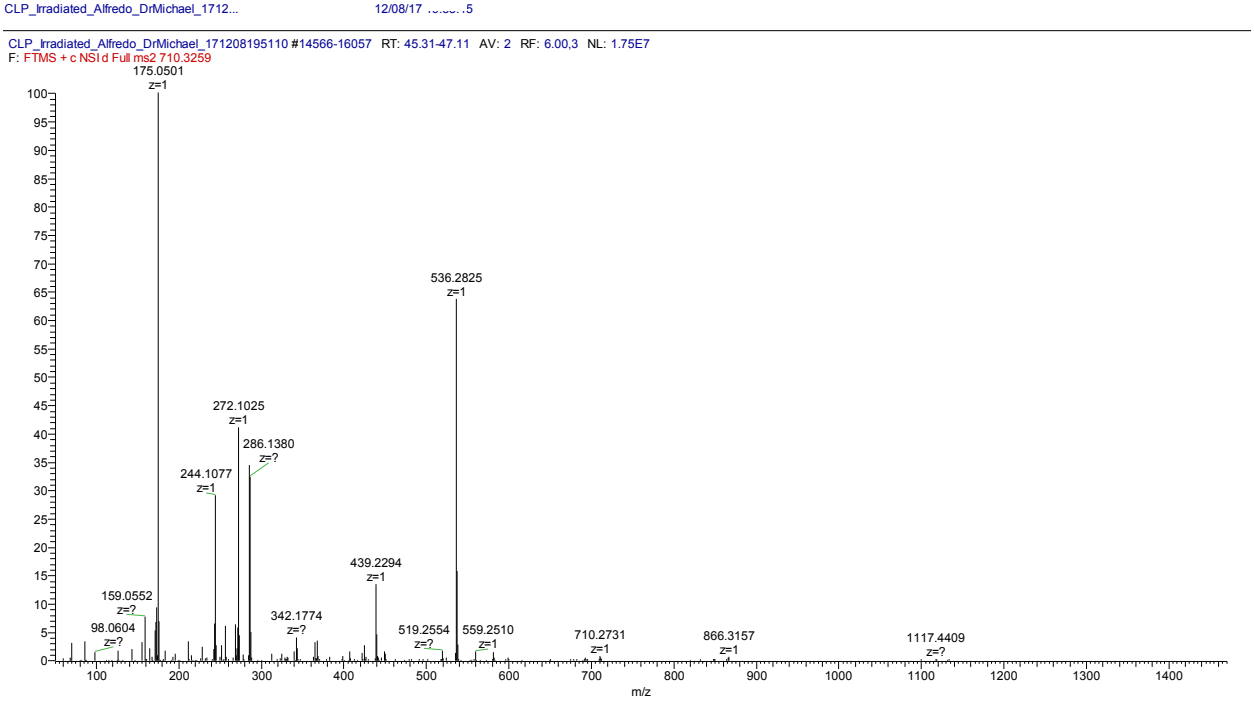


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

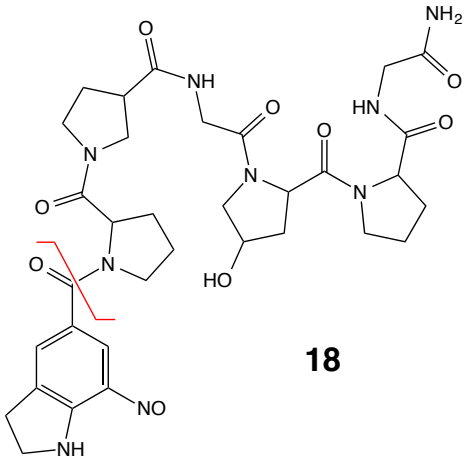
Bottom: HRMS of peptide **18** eluting at 45.47 min: *m/z* $[M+H]^+$ calcd. 710.3262, obs. 710.3259; *m/z* $[M+2H]^{2+}$ calcd. 355.6670, obs. 355.6664.



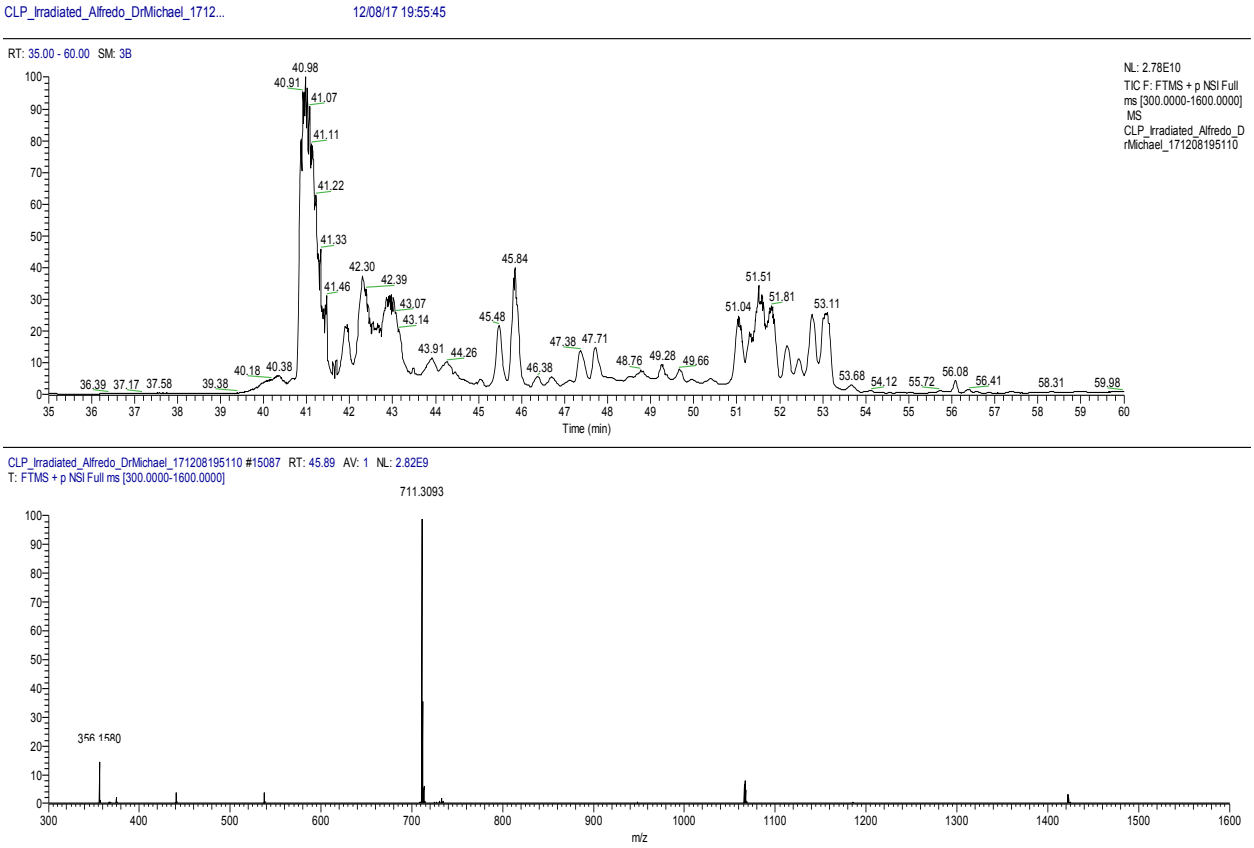
18



MS/MS spectrum of peptide **18**: N-terminal nitrosoindoline fragment, $C_9H_7N_2O_2$, *m/z* $[M]^+$ calcd. 175.0508, obs. 175.0501; protonated C-terminal fragment, $C_{24}H_{38}N_7O_7$, *m/z* $[M+H]^+$ calcd. 536.2833, obs. 536.2835.

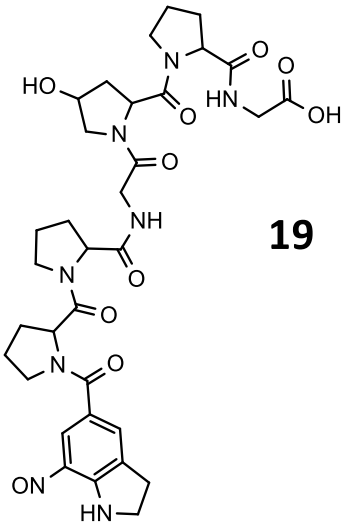


18

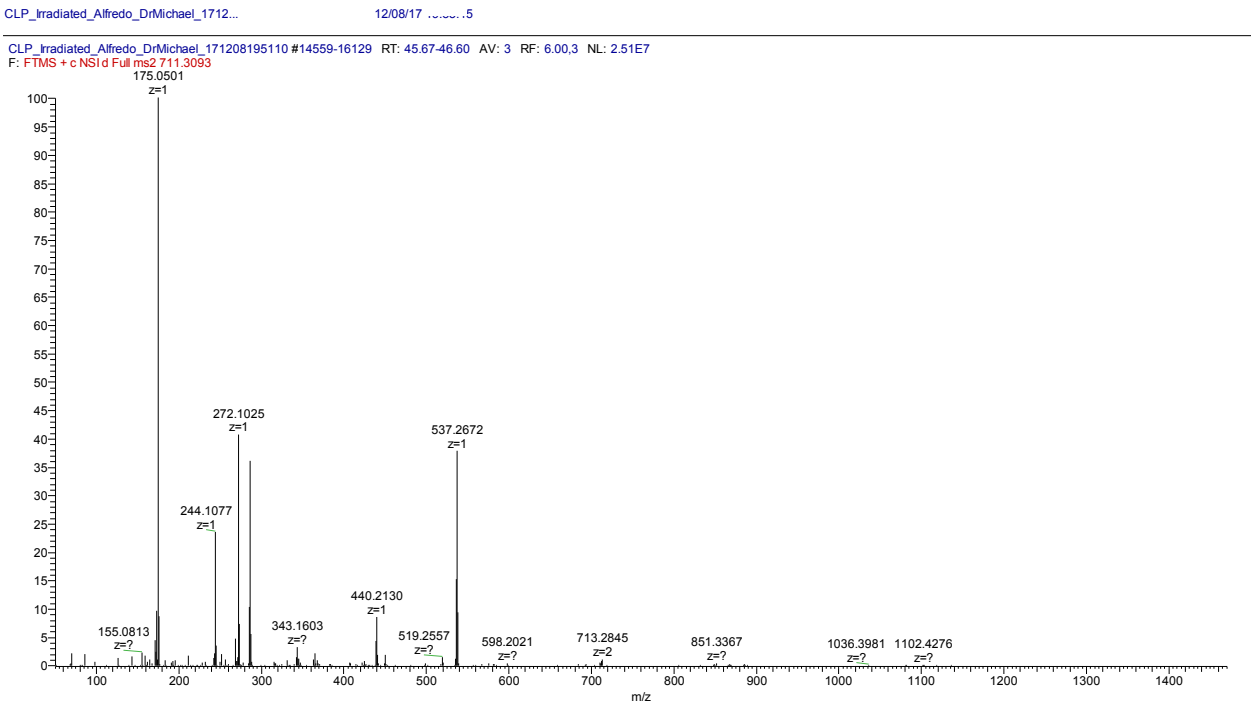


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

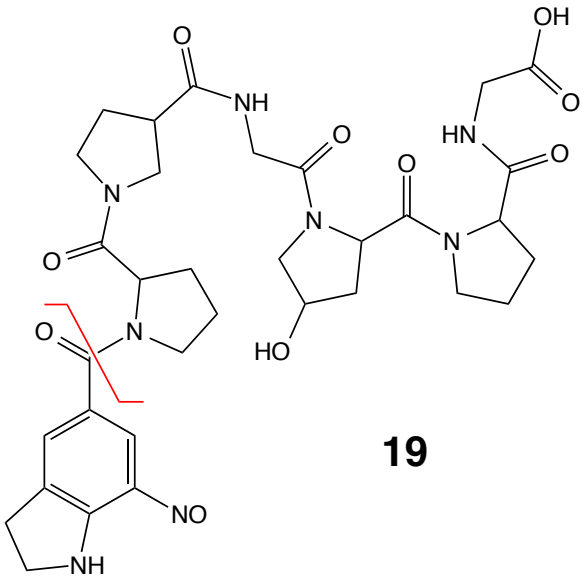
Bottom: HRMS of peptide **19** eluting at 45.89 min: *m/z* $[M+H]^+$ calcd. 711.3102, obs. 711.3093; *m/z* $[M+H]^{2+}$ calcd. 356.1590, obs. 356.1580.



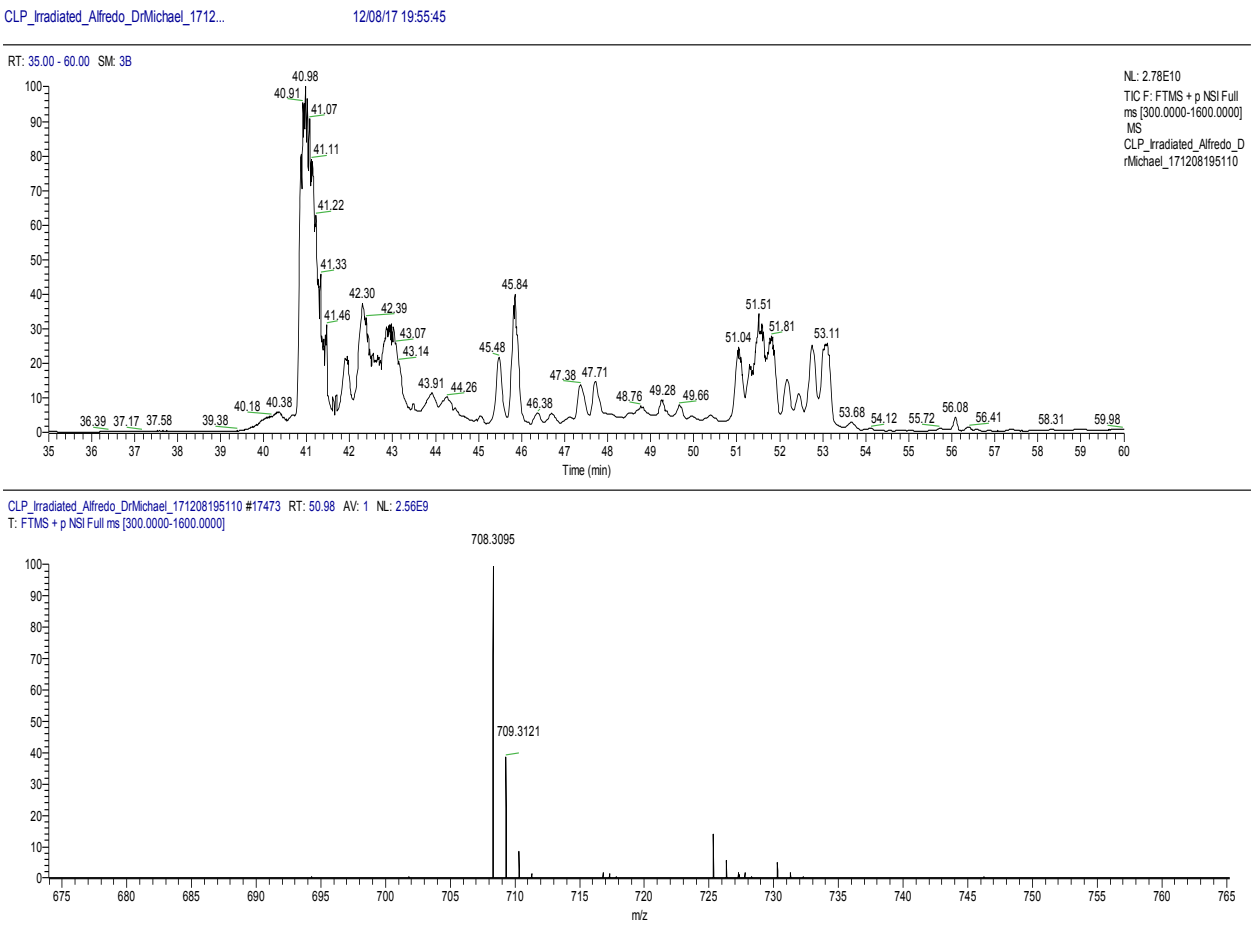
19



MS/MS spectrum of peptide **19**: N-terminal nitrosoindoline fragment, $C_9H_7N_2O_2$, *m/z* $[M]^+$ calcd. 175.0508, obs. 175.0501; protonated C-terminal fragment, $C_{24}H_{37}N_6O_8$, *m/z* $[M+H]^+$ calcd. 537.2673, obs. 537.2672.

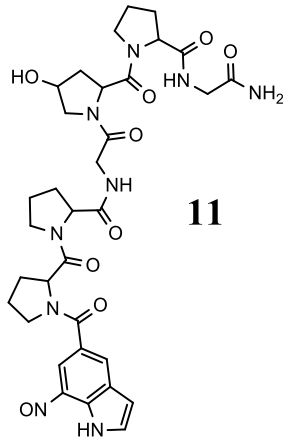


19

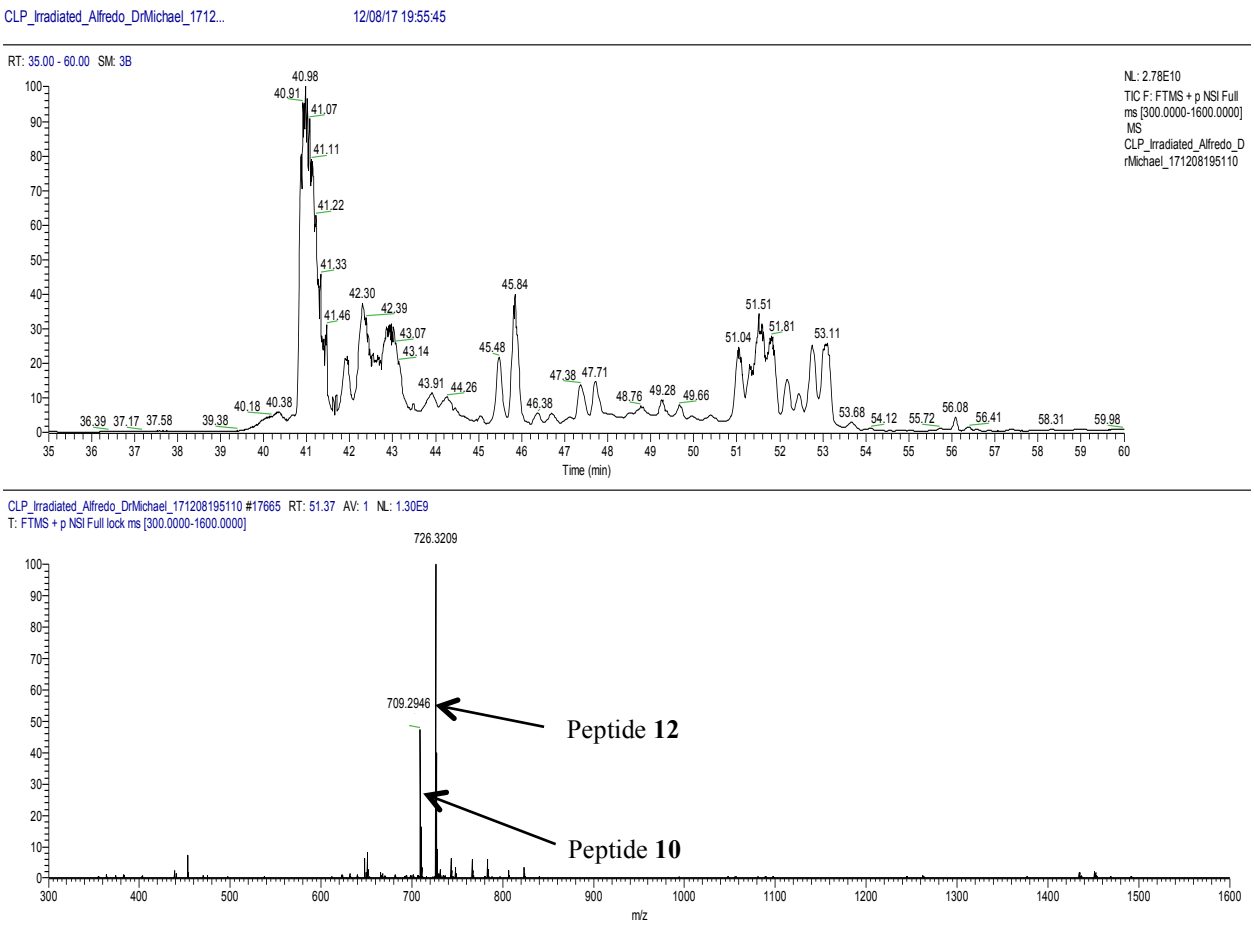


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptide **11** eluting at 50.98 min: *m/z* $[M+H]^+$ calcd. 708.3105, obs. 708.3095.

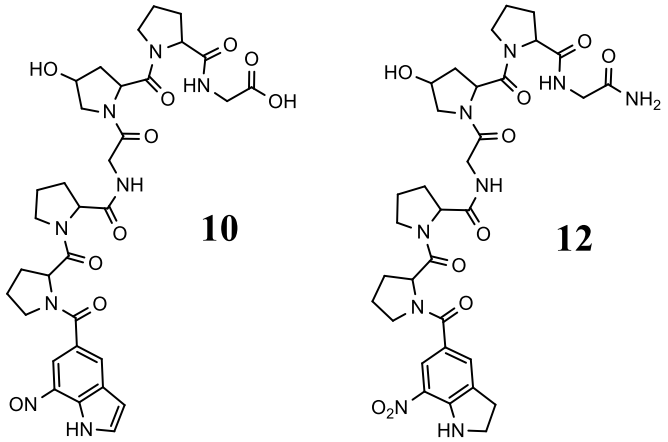


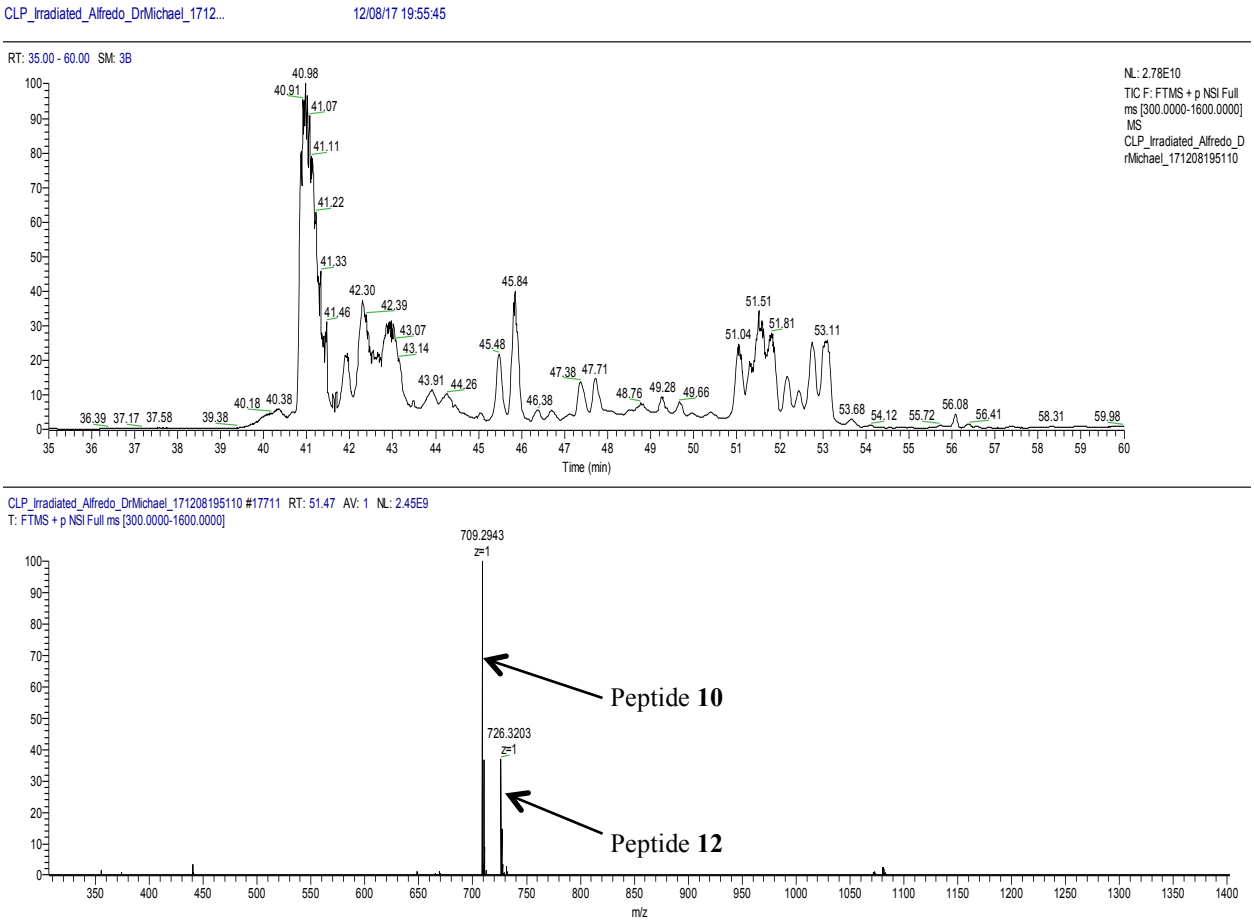
11



Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

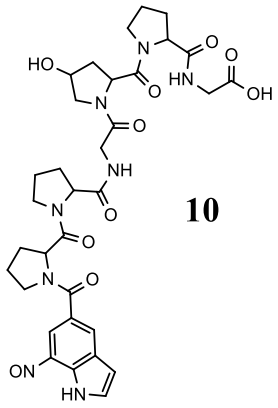
Bottom: HRMS of peptides **10** and **12** eluting at 51.37 min: **10**, *m/z* $[M+H]^+$ calcd. 709.2946, obs. 709.2946; **12**, *m/z* $[M+H]^+$ calcd. 726.3211, obs. 726.3209.



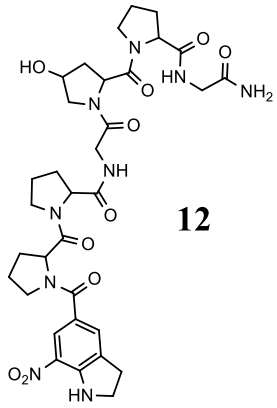


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

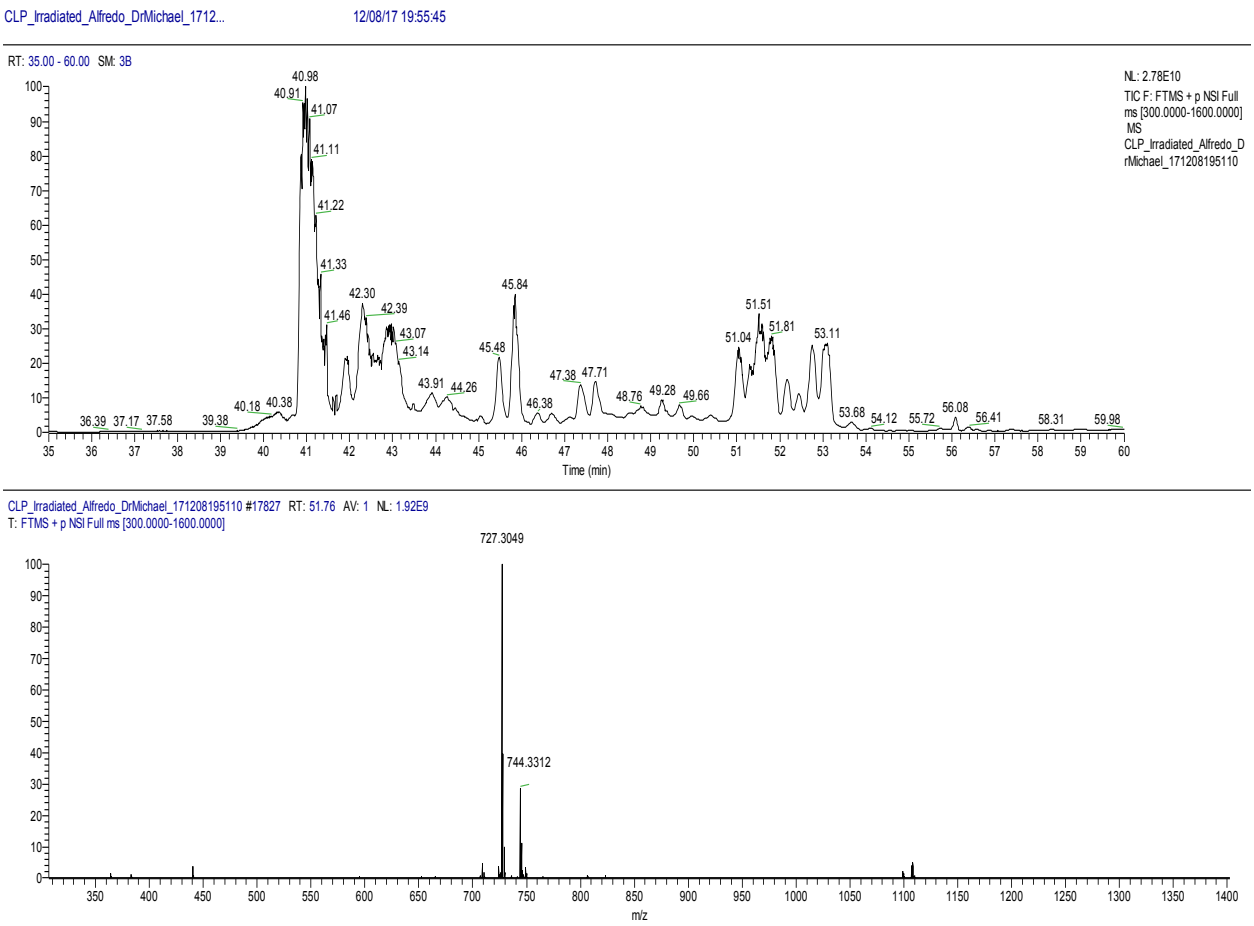
Bottom: HRMS of peptides **10** and **12** eluting at 51.47 min: **10**, *m/z* $[M+H]^+$ calcd. 709.2946, obs. 709.2943; **12**, *m/z* $[M+H]^+$ calcd. 726.3211, obs. 726.3203.



10

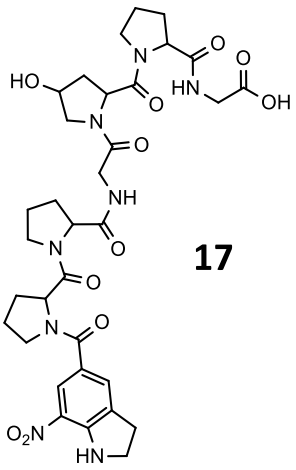


12

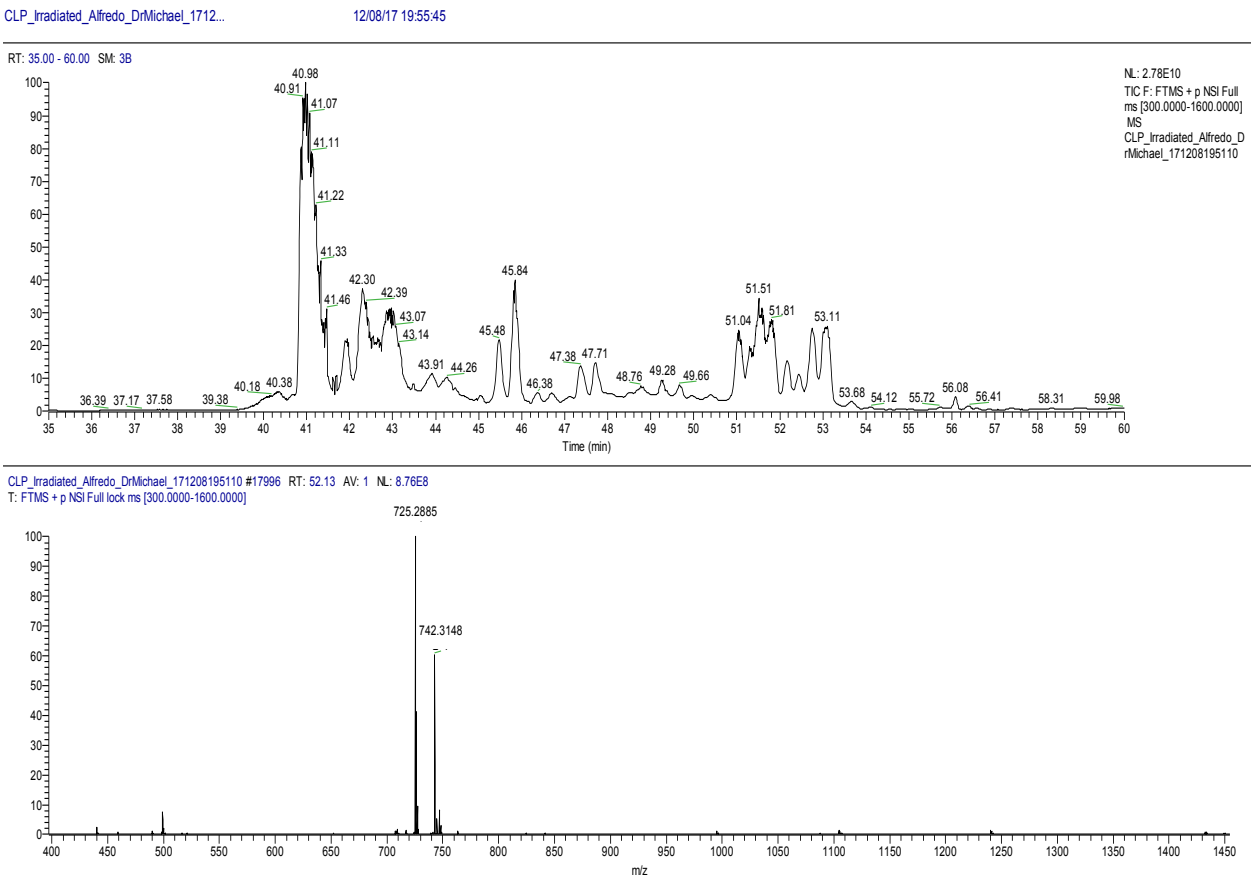


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

Bottom: HRMS of peptide **17** eluting at 51.76 min: *m/z* $[M+H]^+$ calcd. 727.3051, obs. 727.3049; *m/z* $[M+NH_4]^+$ calcd. 744.3317, obs. 744.3312.

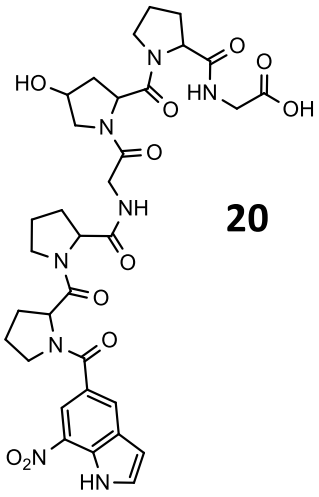


17

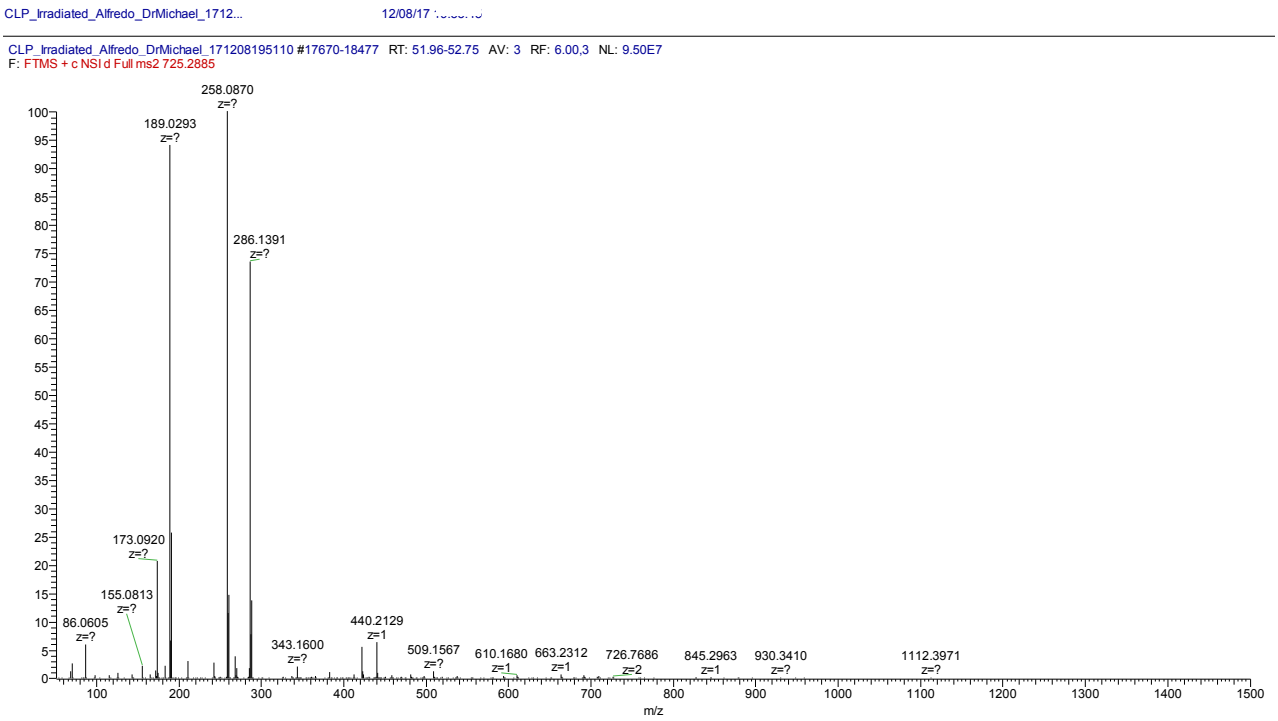


Top: TIC chromatogram of photolysis products of peptide **1**, irradiated with near UV light (350 nm) in water.

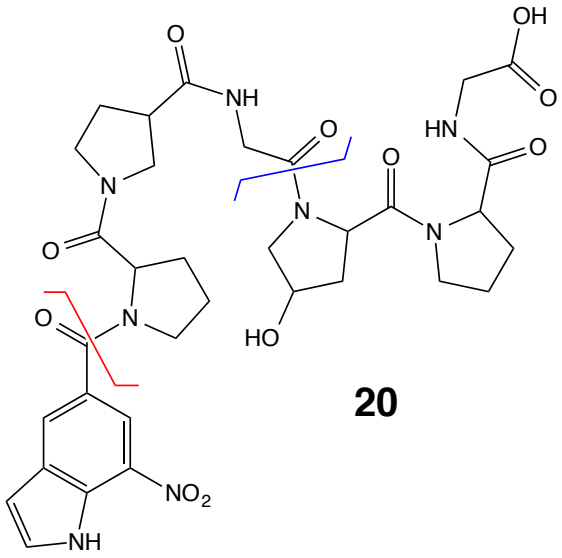
Bottom: HRMS of peptide **20** eluting at 52.13 min: *m/z* $[M+H]^+$ calcd. 725.2895, obs. 725.2885; *m/z* $[M+NH_4]^+$ calcd. 742.3160, obs. 742.3148.



20



MS/MS spectrum of peptide **20**: N-terminal nitroindole fragment, $C_9H_5N_2O_3$, *m/z* $[M]^+$ calcd. 189.0300 , obs. 189.0293; protonated C-terminal tripeptide fragment, $C_{12}H_{20}N_3O_5$, *m/z* $[M+H]^+$ calcd. 286.1403, obs. 286.1391.



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