

Supplemental Data

Mechanistic details of the mycofactocin biosynthetic protein MftC, a radical-S-adenosylmethionine protein.

Bulat Khaliullin¹, Richard Ayikpoe¹, Mason Tuttle¹, John A. Latham^{1†}

¹Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, USA.

† Address correspondence to John Latham, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208. E-mail: john.latham@du.edu; Tel. +1 303 871 2533; Fax. +1 303 871 2254

Figure S1. Mass spectra of (A) MftA M1W purified peptide, (B) MftA M1W product 1 (MftA*) and (C) MftA M1W product 2 (MftA**). All collected spectral data are represented in black and the predicted spectra for the MH³⁺ ions are shown in red.

Figure S2. Mass spectrum of (A) ¹³C₉, ¹⁵N tyrosine labeled MftA M1W purified peptide and (B) purified ¹³C₉, ¹⁵N tyrosine labeled MftA M1W*. All collected spectral data are represented in black and the predicted spectra for the MH³⁺ ions are shown in red.

Figure S3. ¹³C NMR spectra for (A) unreacted ¹³C₉, ¹⁵N tyrosine labeled MftA M1W and (B) the ¹³C₉, ¹⁵N tyrosine labeled MftA M1W* product. ¹H NMR spectra for (C) unreacted MftA M1W and (D) the MftA M1W* product.

Figure S4. ¹³C NMR spectra for (A) *Z*-L-Val-*p*-(2-aminoethenyl)phenol and (B) *E*-L-Val-*p*-(2-aminoethenyl)phenol. ¹H NMR spectra for (C) *Z*-L-Val-*p*-(2-aminoethenyl)phenol and (D) *E*-L-Val-*p*-(2-aminoethenyl)phenol.

Figure S5. UV-Vis spectra for (red) *E*-L-Val-*p*-(2-aminoethenyl)phenol (140 μM) and (blue) *Z*-L-Val-*p*-(2-aminoethenyl)phenol (110 μM).

Figure S6. Mass spectrum of (A) MftA M1W/V29A purified peptide, (B) MftA M1W/V29A**. All collected spectral data are represented in black and the predicted spectra for the MH³⁺ ions are shown in red. (C) ¹H NMR spectra for reacted MftA M1W/V29A**.

Figure S7. Mass spectrum of (A) tyrosine Ring-2,6-D₂, 2-D MftA M1W (C_α-labeled), (B) tyrosine 3,3-2D, MftA M1W (C_β-labeled).

Scheme S1. Reaction scheme for the synthesis of *Z*-L-Val-*p*-(2-aminoethenyl)phenol.

Scheme S2. Reaction scheme for the synthesis of *E*-L-Val-*p*-(2-aminoethenyl)phenol.

Figure S1.

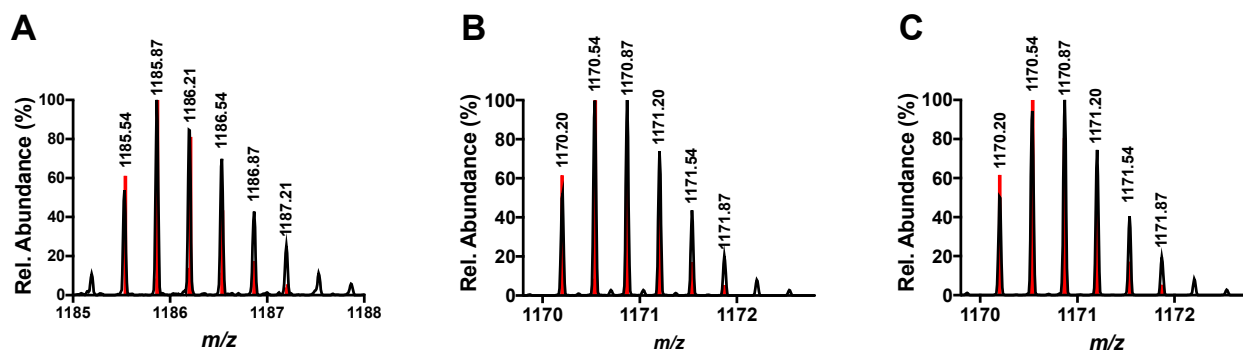


Figure S2.

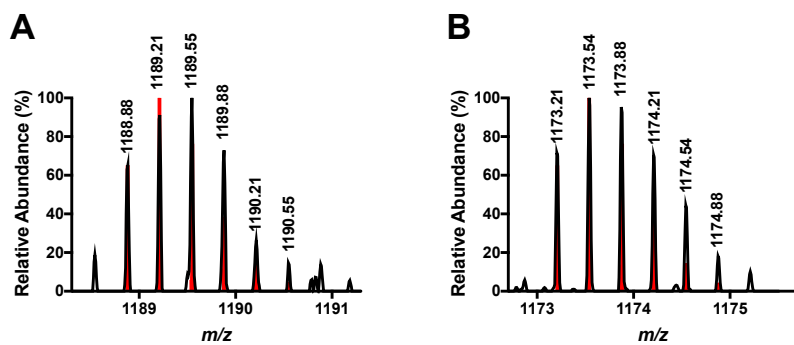
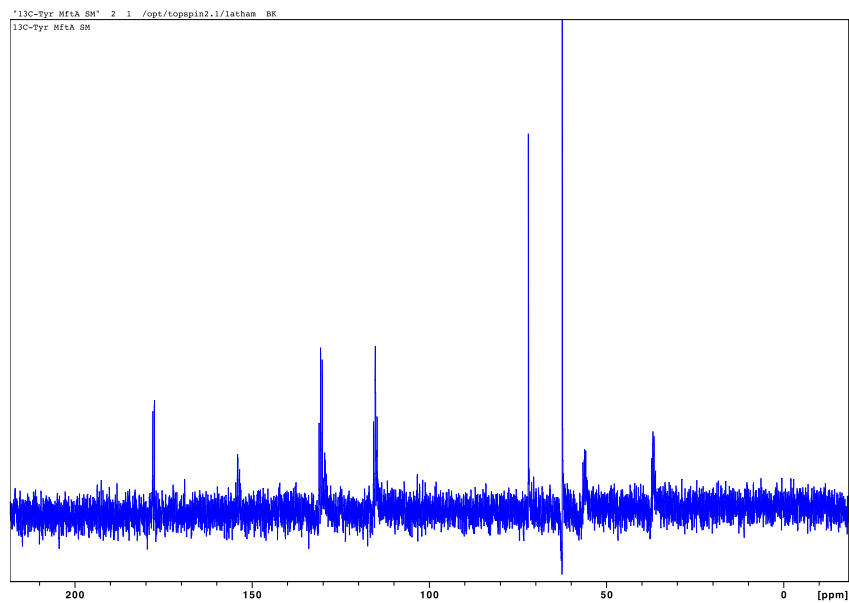
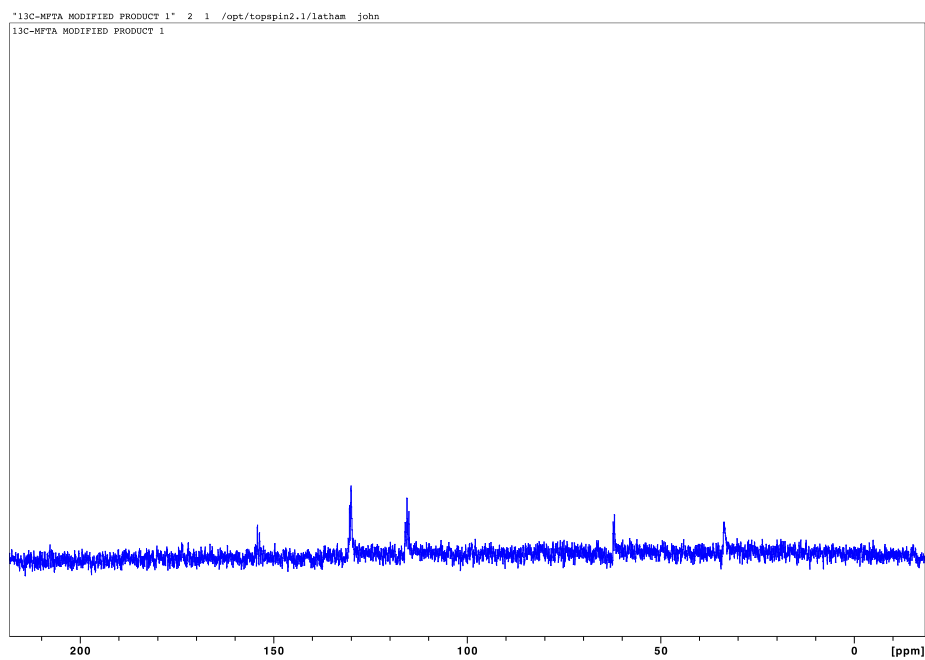


Figure S3.

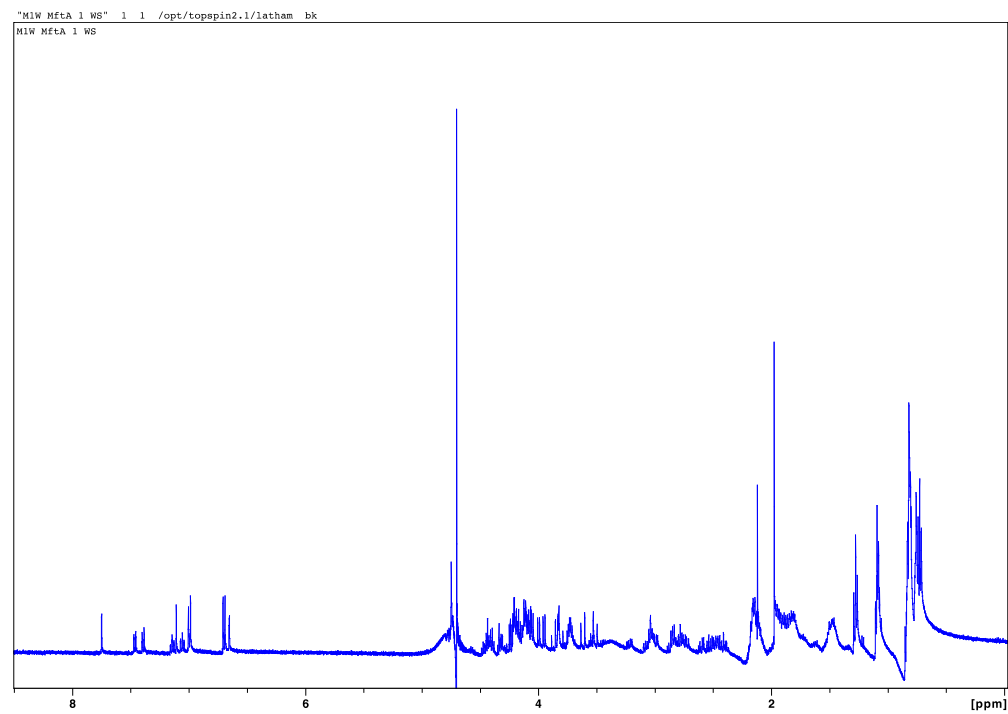
A.



B.



C.



D.

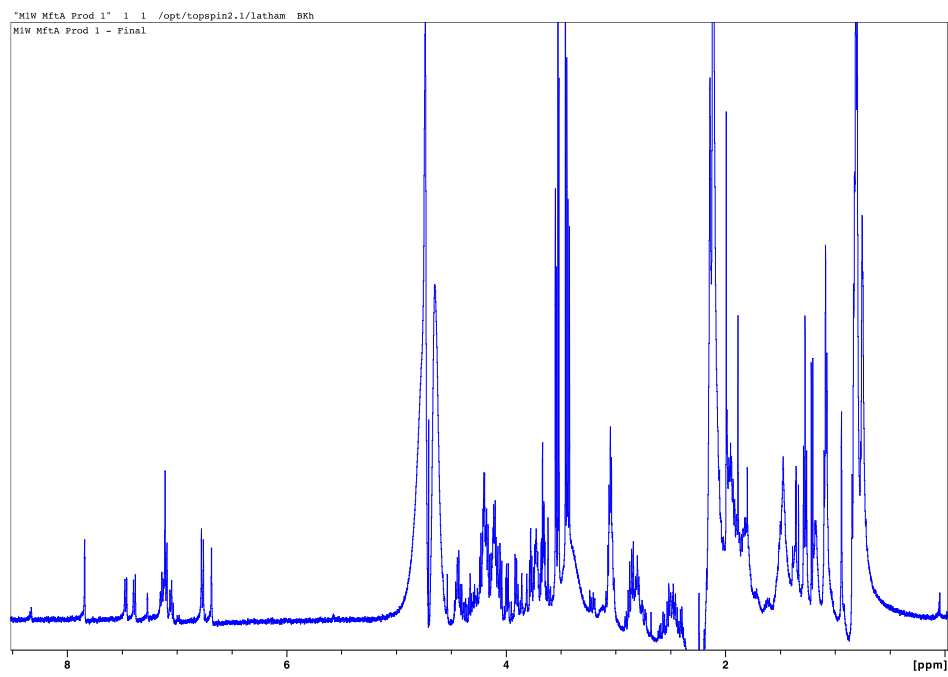
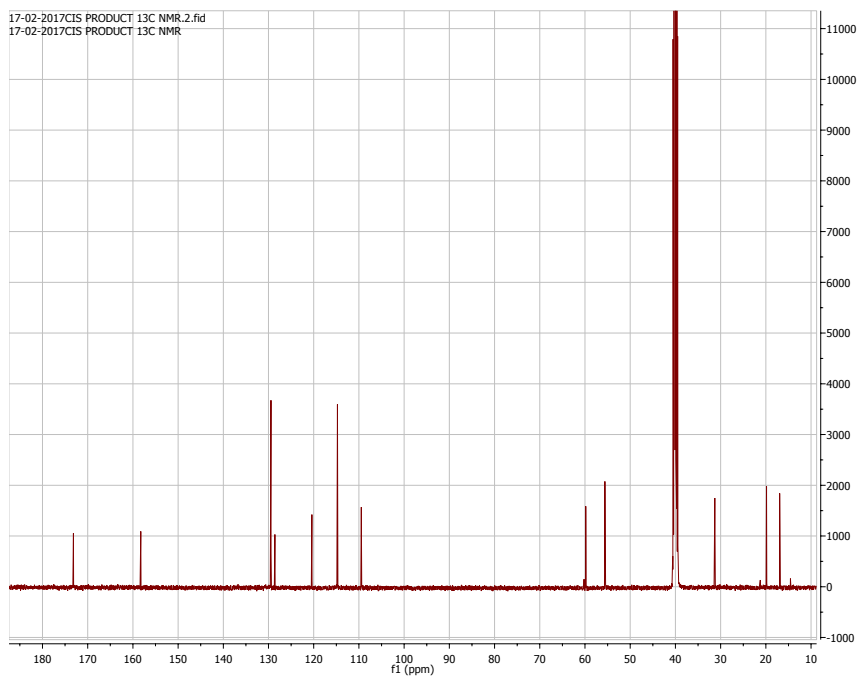
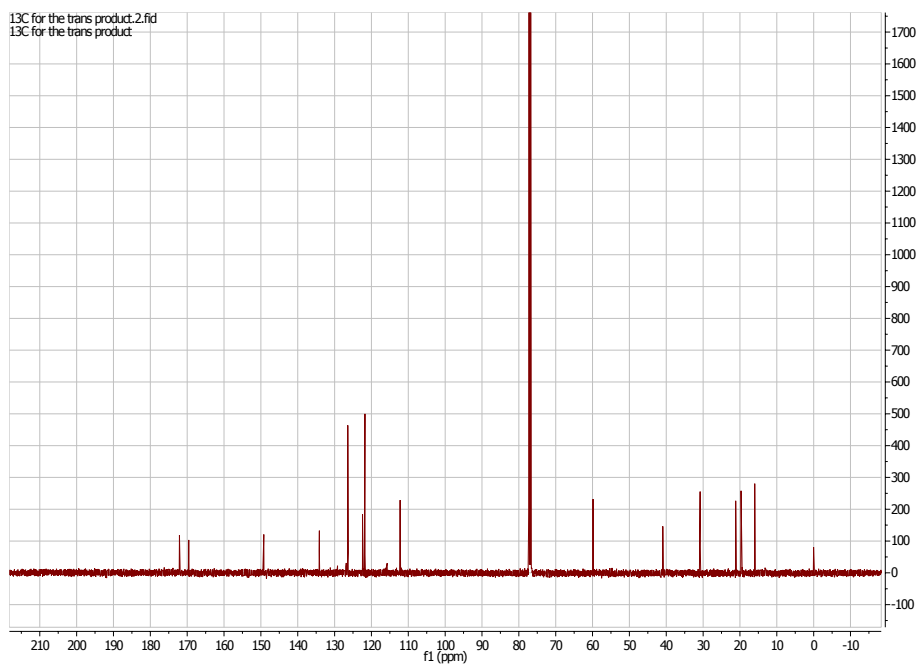


Figure S4.

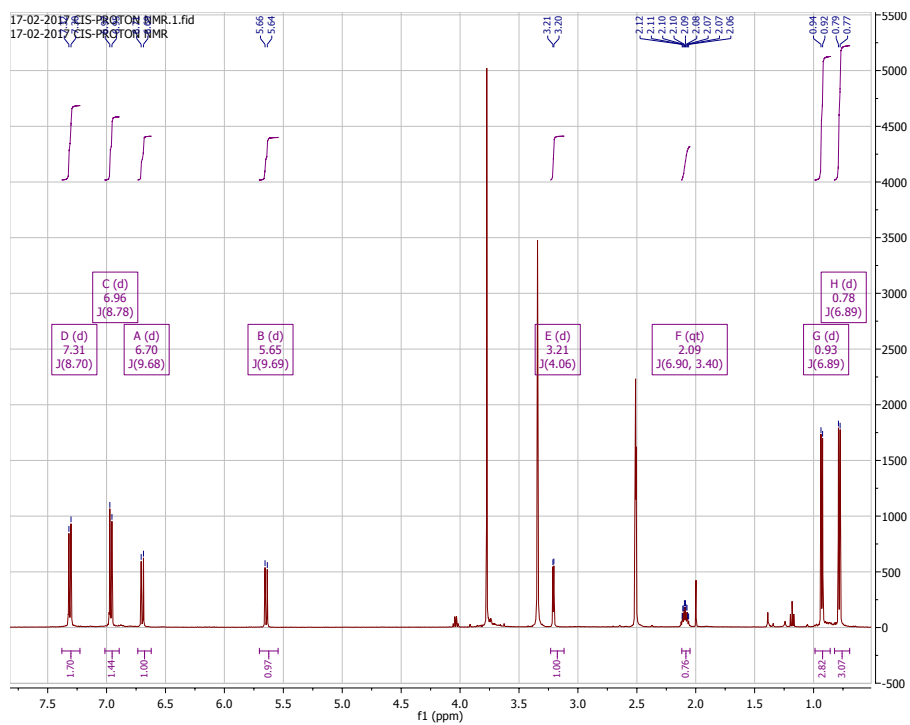
A.



B.



C.



D.

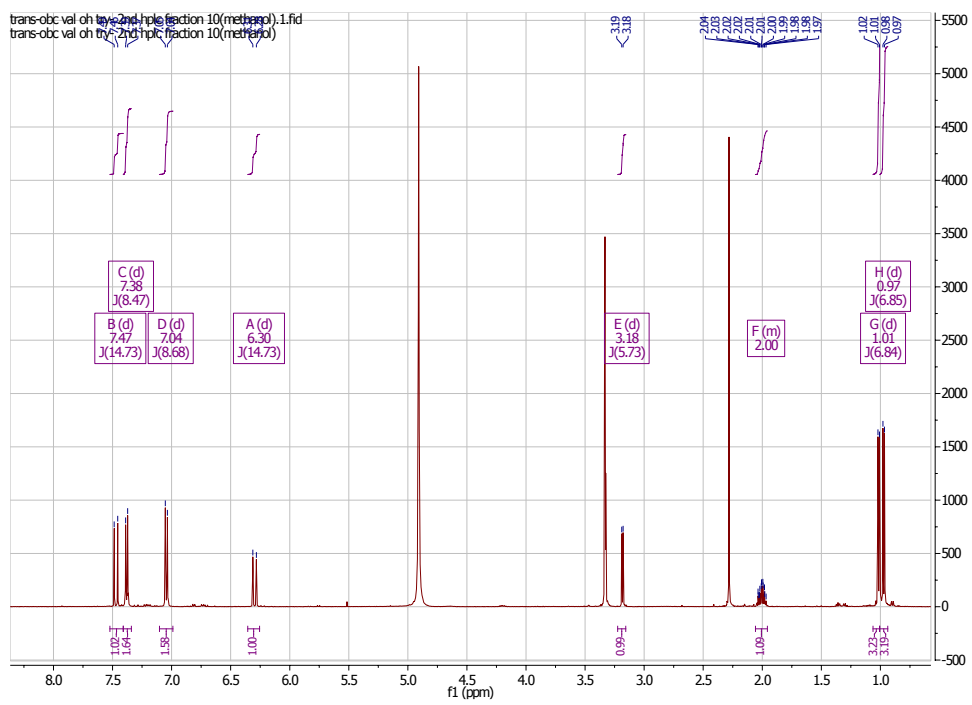


Figure S5.

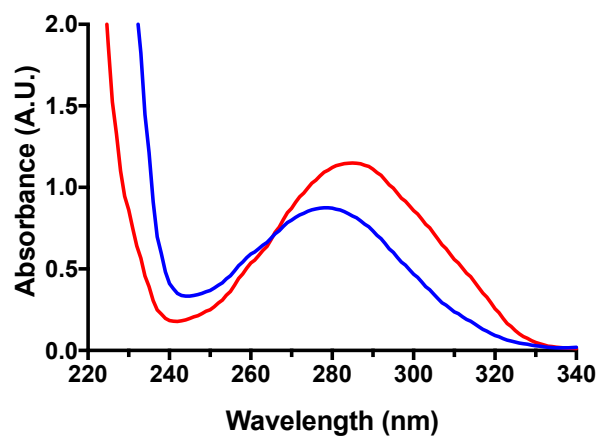
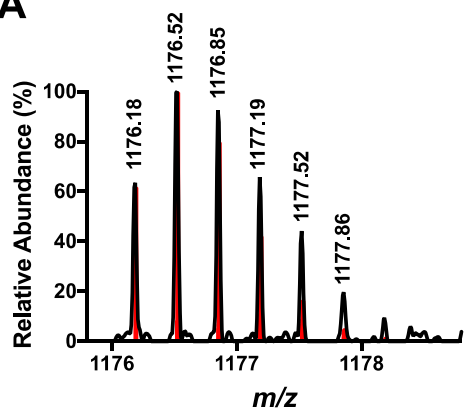
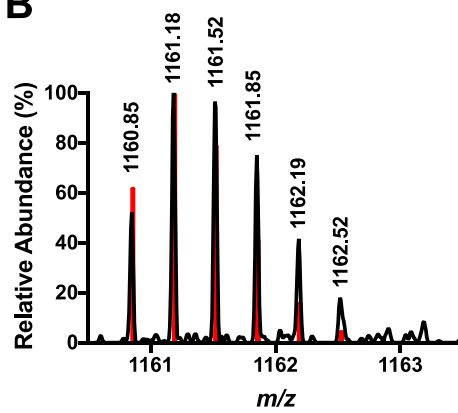


Figure S6

A



B



C

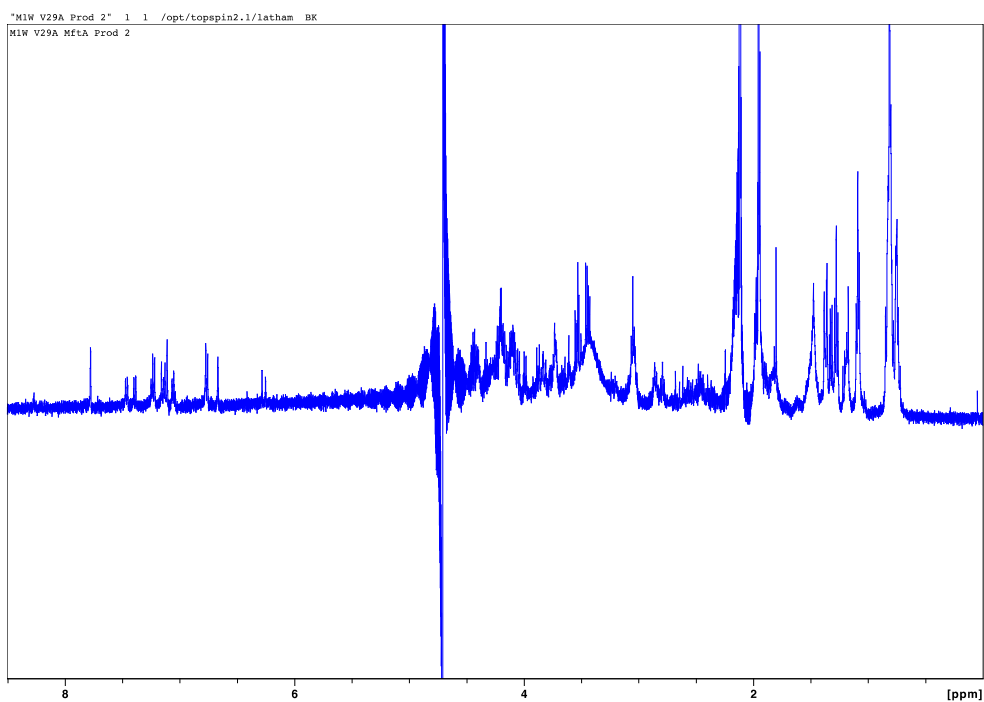
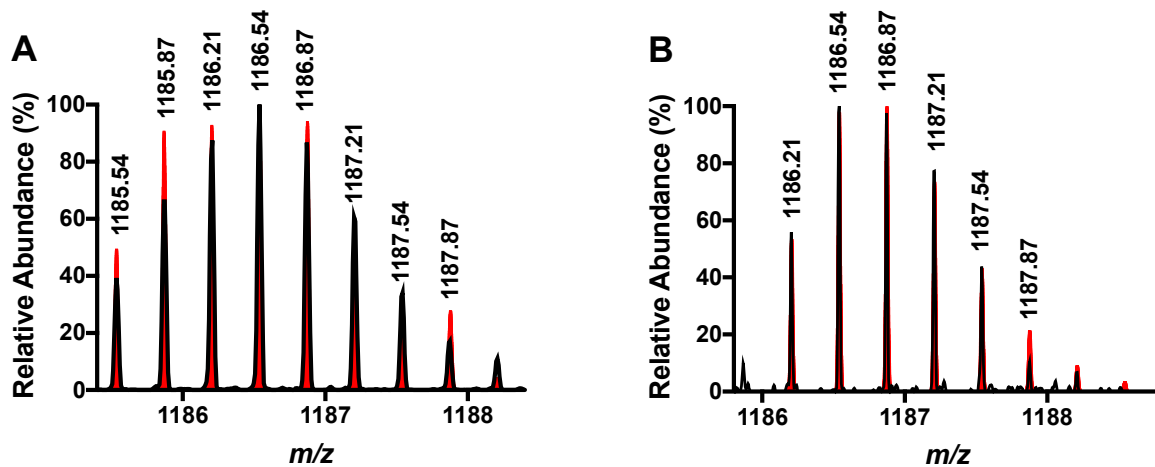
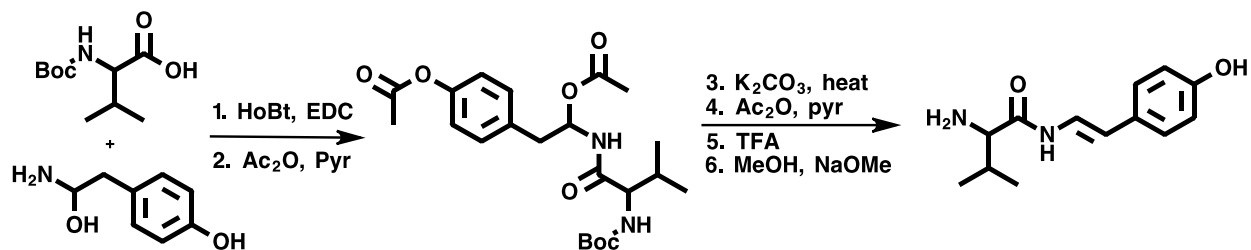


Figure S7.



Scheme S1.



Scheme S2.

