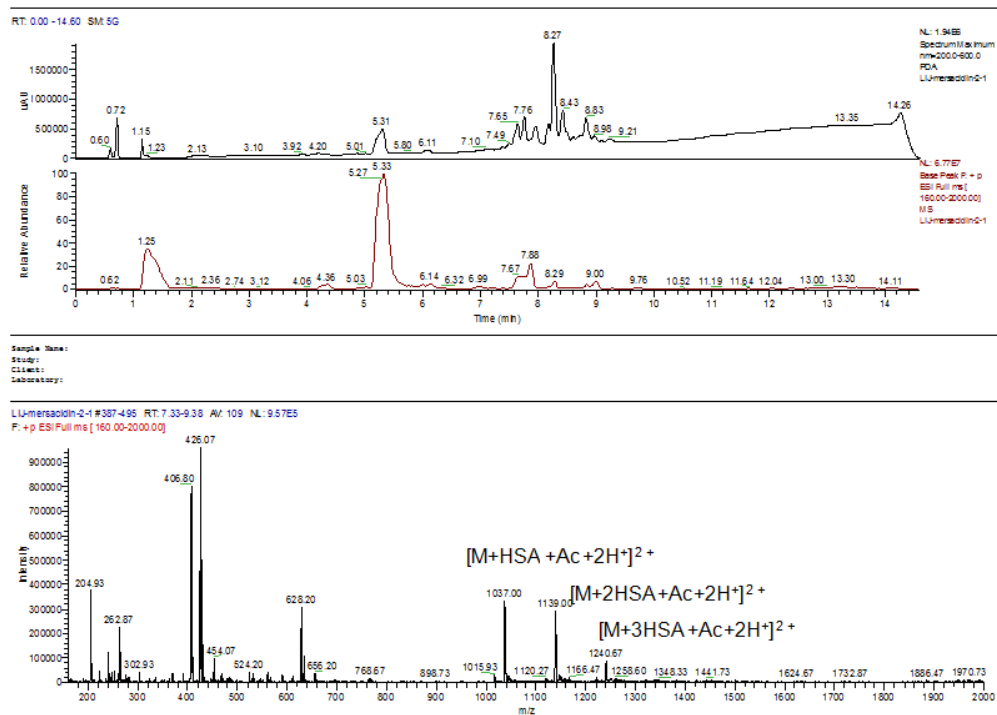


## Supplemental Figures



5 **Figure 1.** LC/MS spectrum after reaction of mersacidin with excess probe 1 under strong basic conditions at elevated temperature for 1 h. gradient: 10% → 90% ACN/0.1% aq. TFA.

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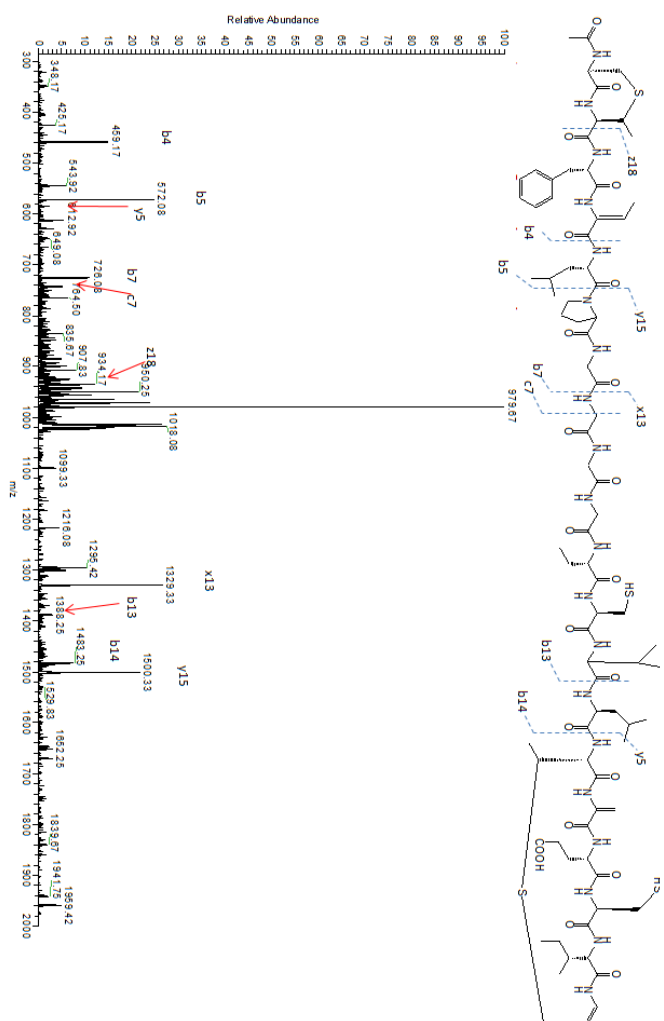
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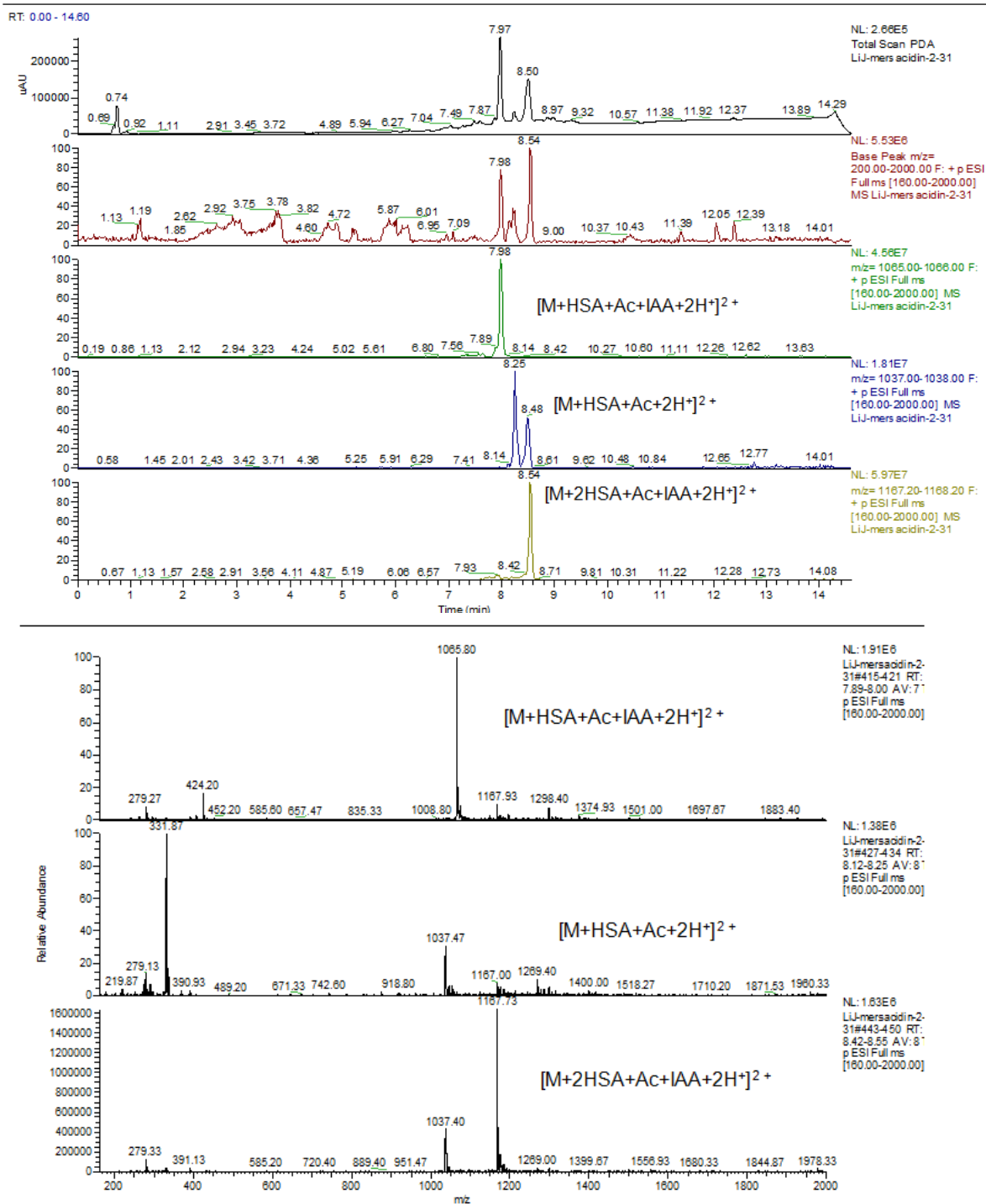
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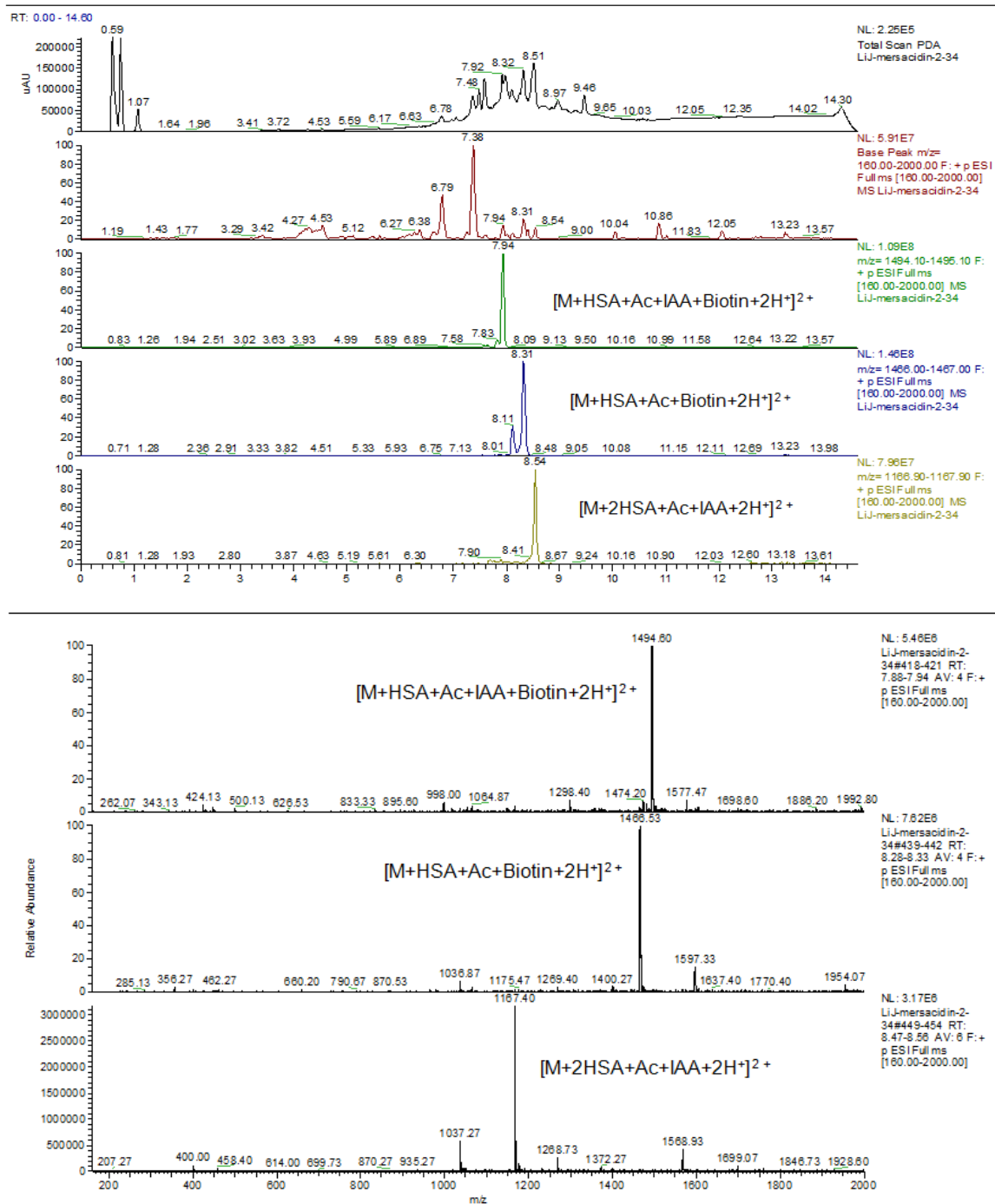
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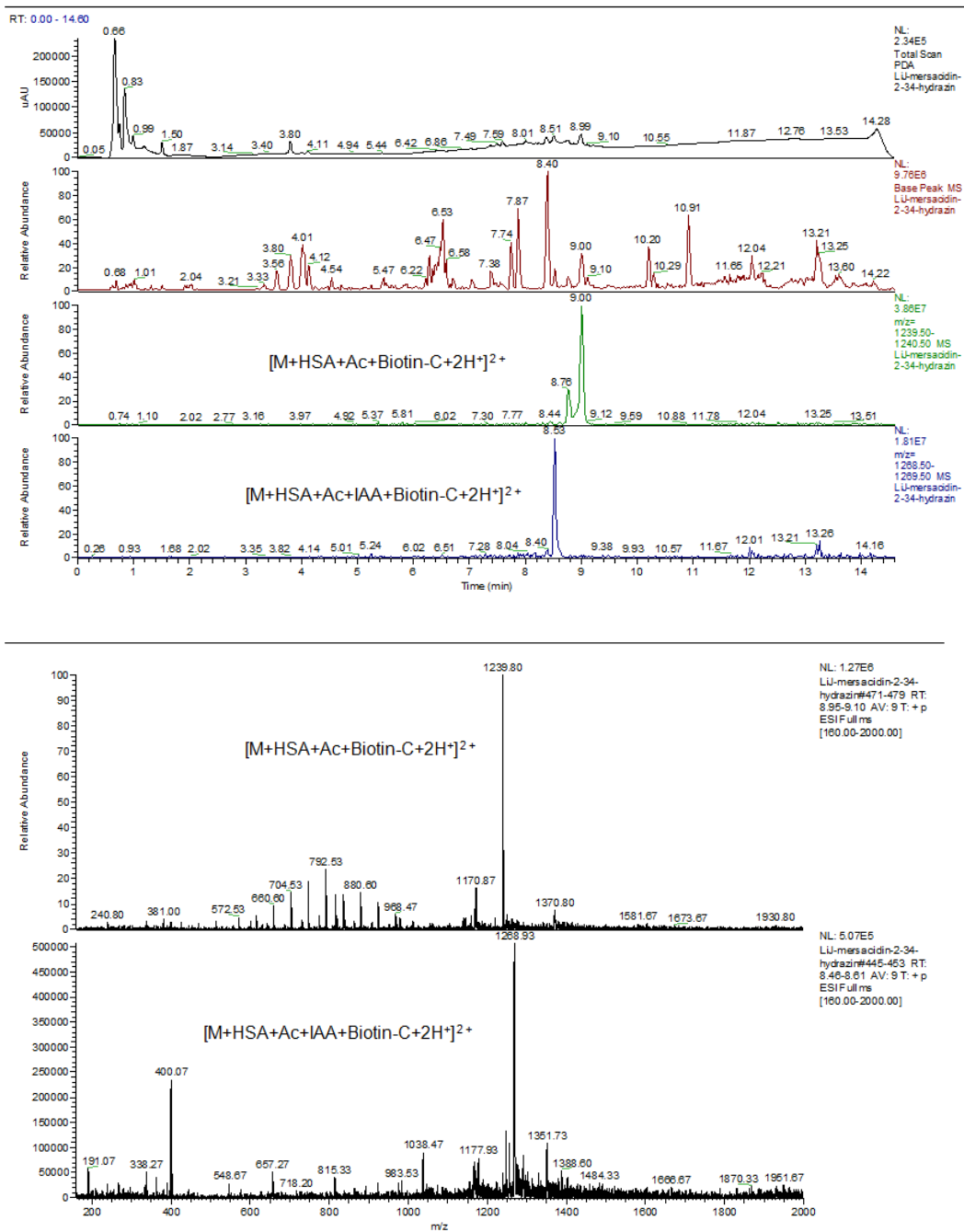
**Figure 2.** MS/MS analysis of the [M+HAS+Ac] and proposed structure of the product.



5 **Figure 3.** LC/MS spectrum of the reaction of mersacidin and thioalkyne (**1**), and DTT treatment followed by reaction with iodoacetamide. gradient: 10% → 90% ACN/0.1% aq. TFA.



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**Figure 4.** LC/MS spectrum of click reaction. gradient: 10% → 90% ACN/0.1% aq. TFA.



5 **Figure 5.** LC/MS spectrum of hydrazine cleavage of the fully labeled sample. Gradient 10% → 90% ACN/0.1% aq. TFA.

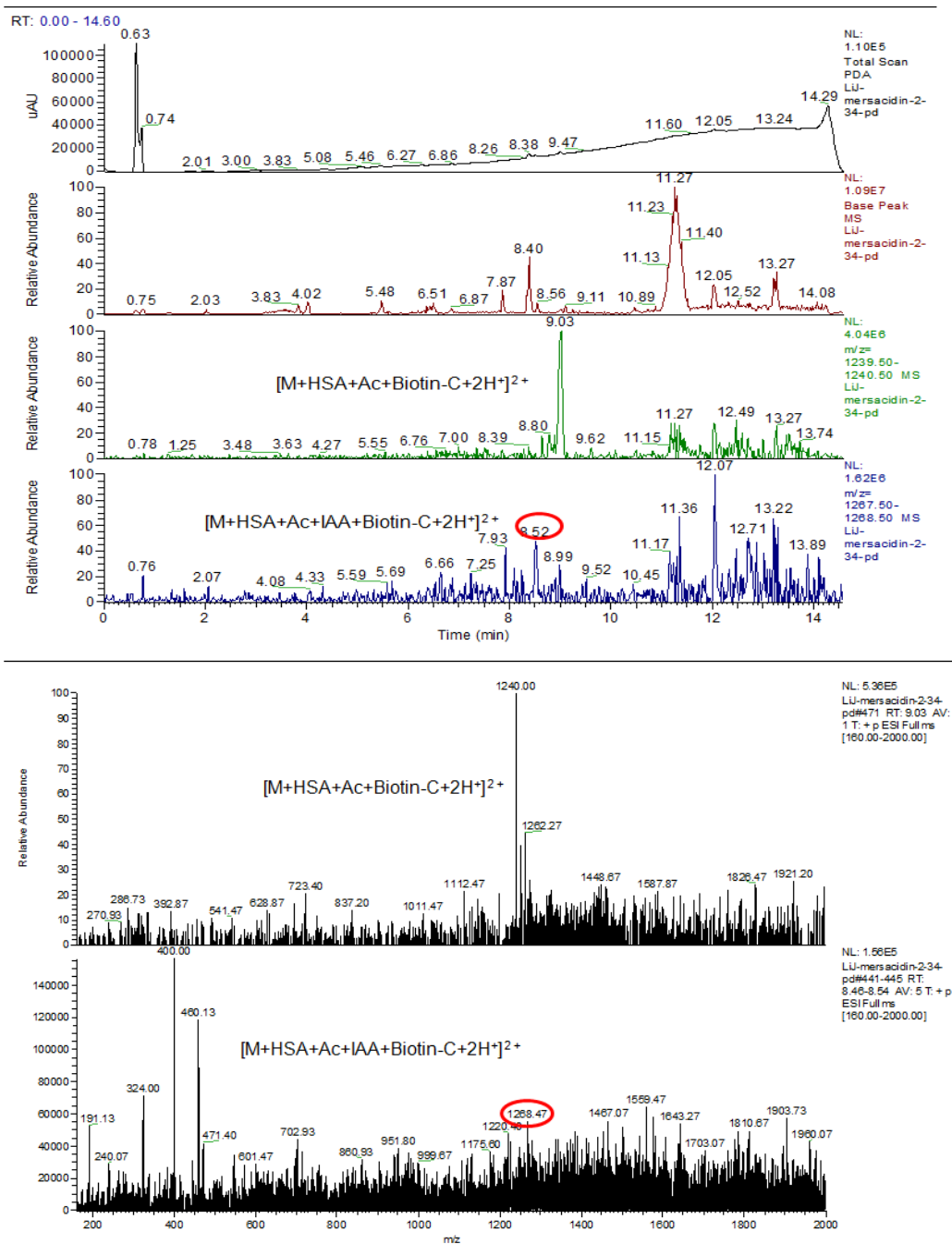
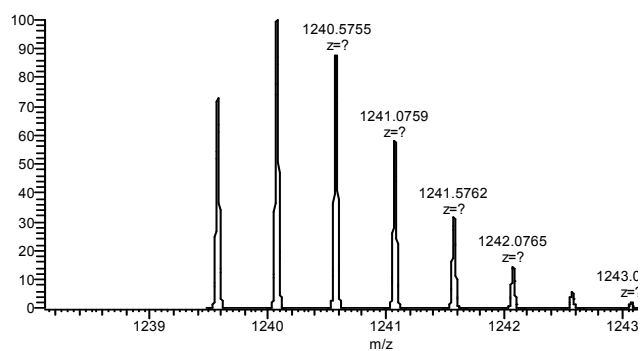
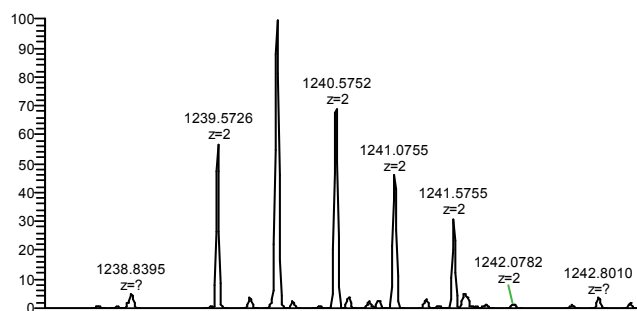


Figure 6. LC/MS of pulled down product obtained after hydrazine treatment. Gradient: 10% → 90% ACN/0.1% aq. TFA.

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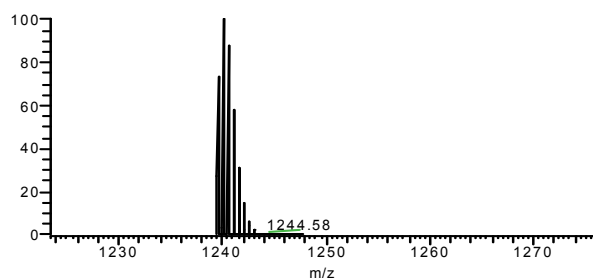
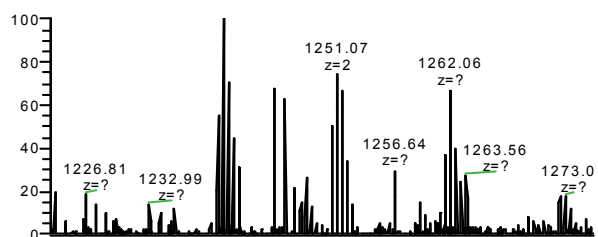


Figure 7. HRMS of modified mersacidin after pull down and hydrazine treatment.