*Electronic Supplementary Information for*

# Stereoselective Synthesis of *Arabidopsis* CLAVATA3 (CLV-3) glycopeptide, unique protein post-translational modifications of secreted peptide hormone in plant

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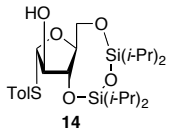
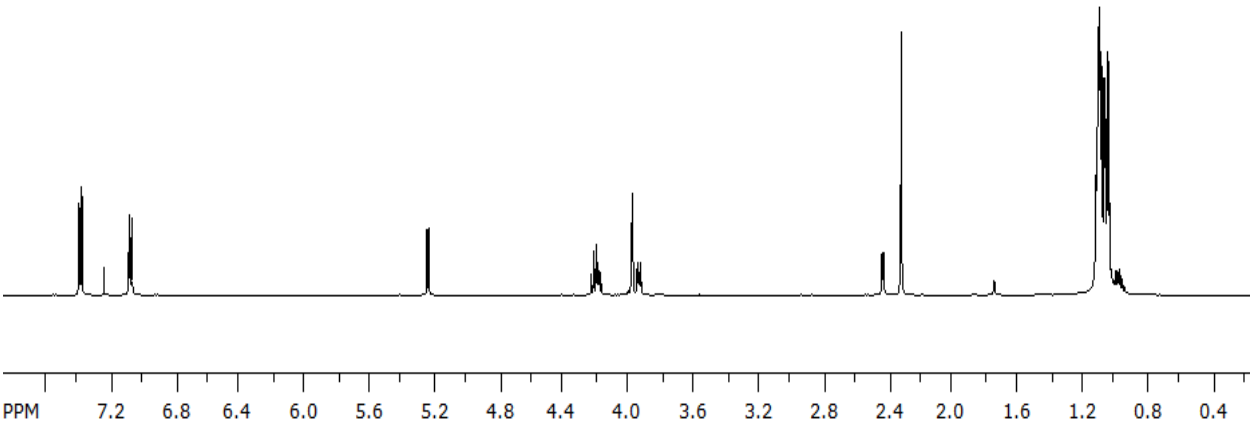
## Contents




**14**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)

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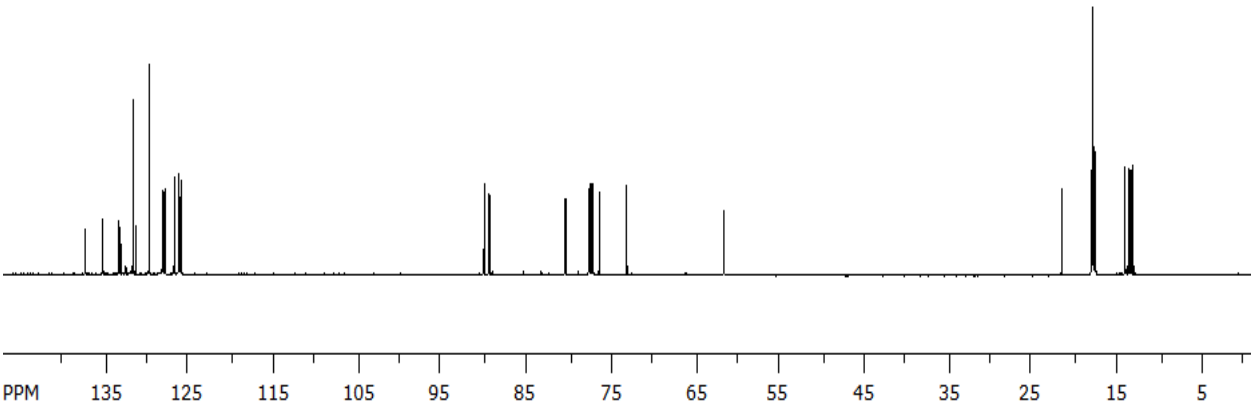

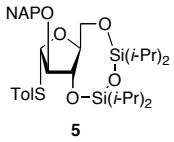


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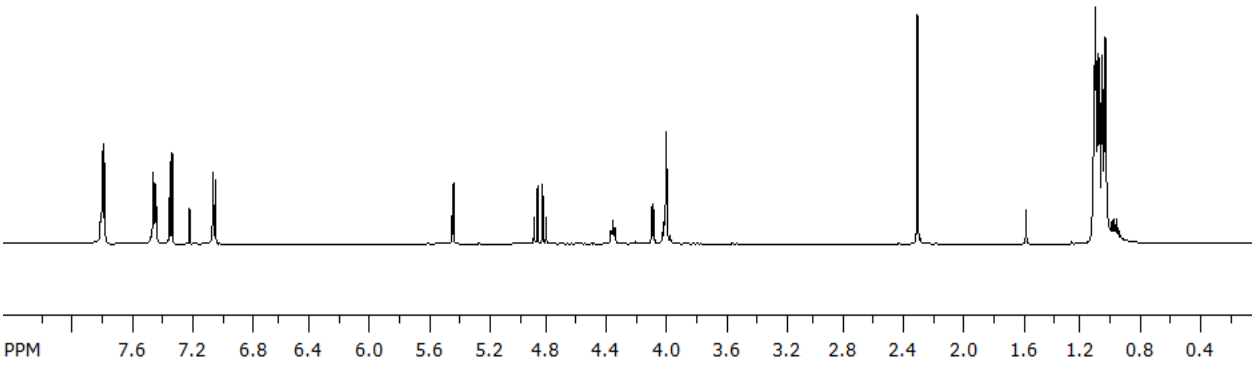


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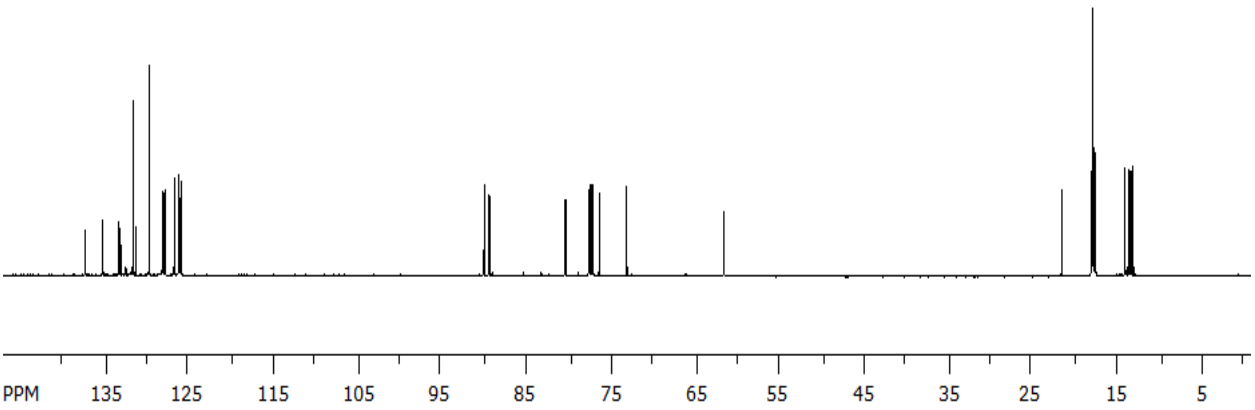

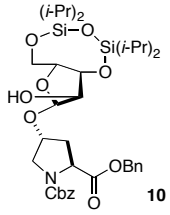


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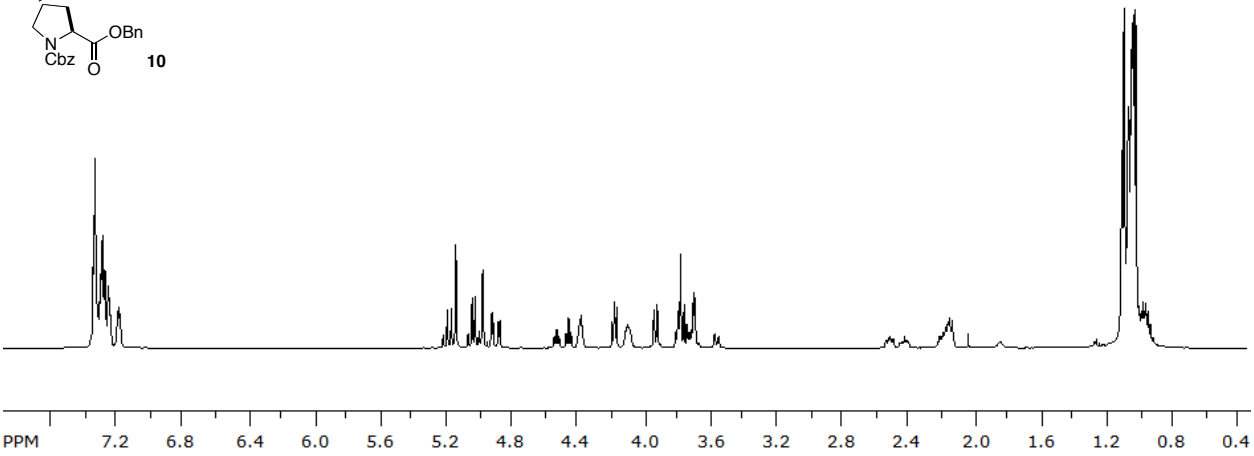


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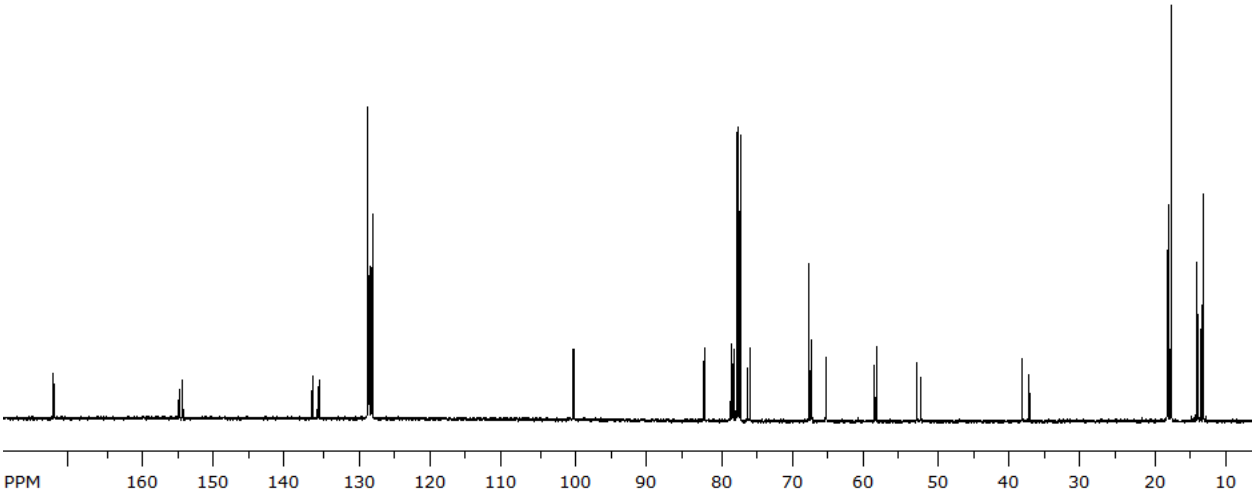

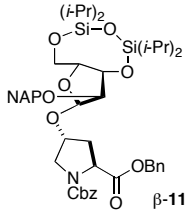

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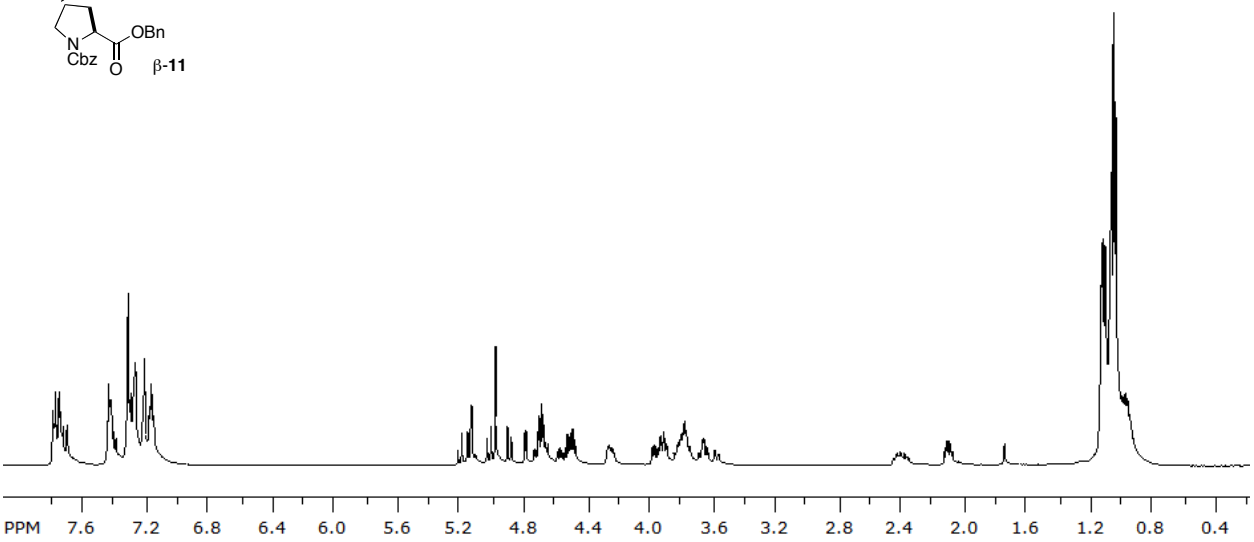


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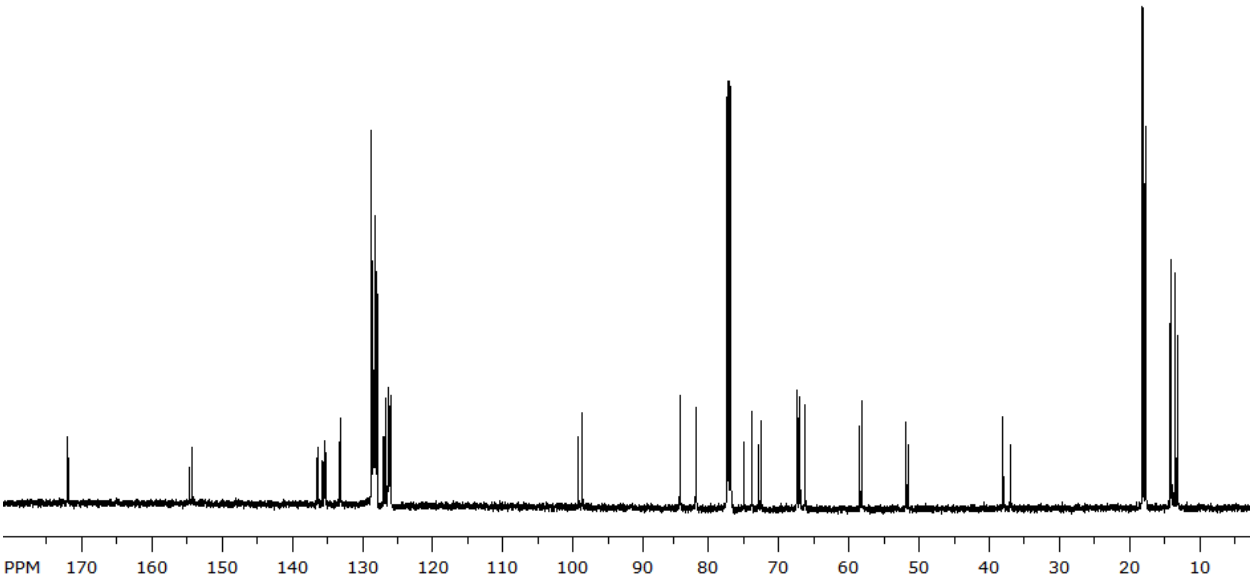
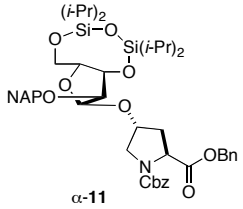


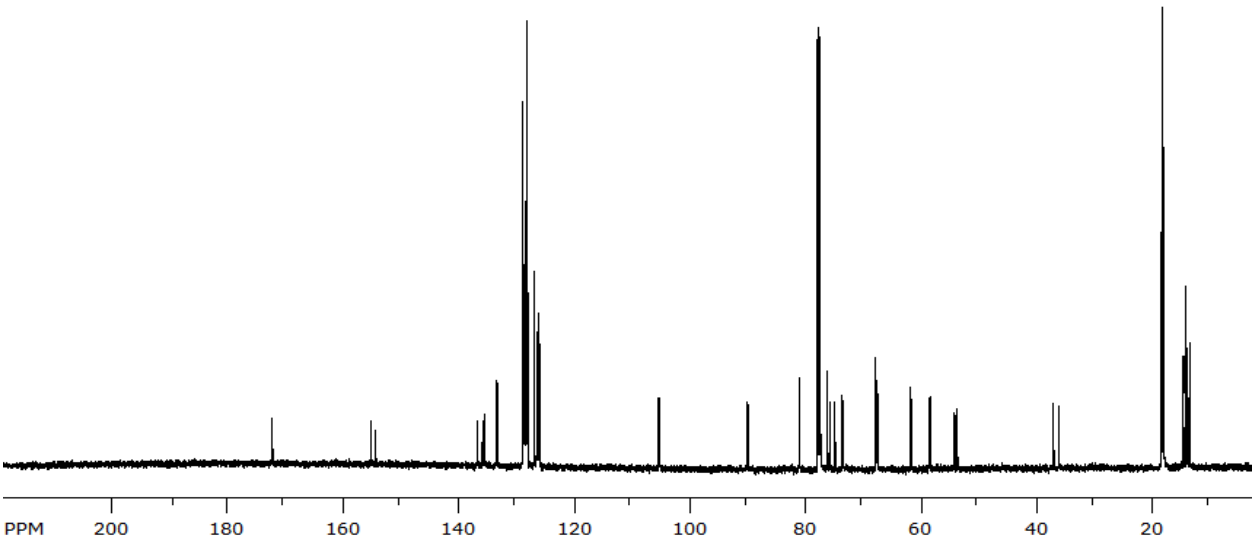


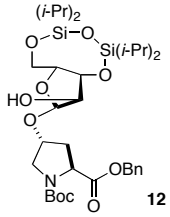
α-**11**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)




**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



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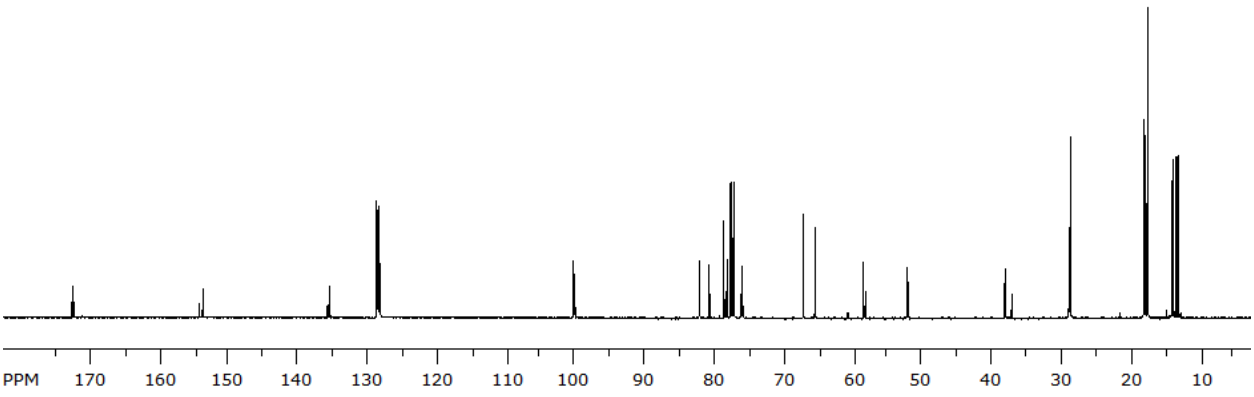
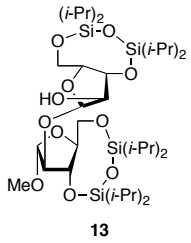
**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



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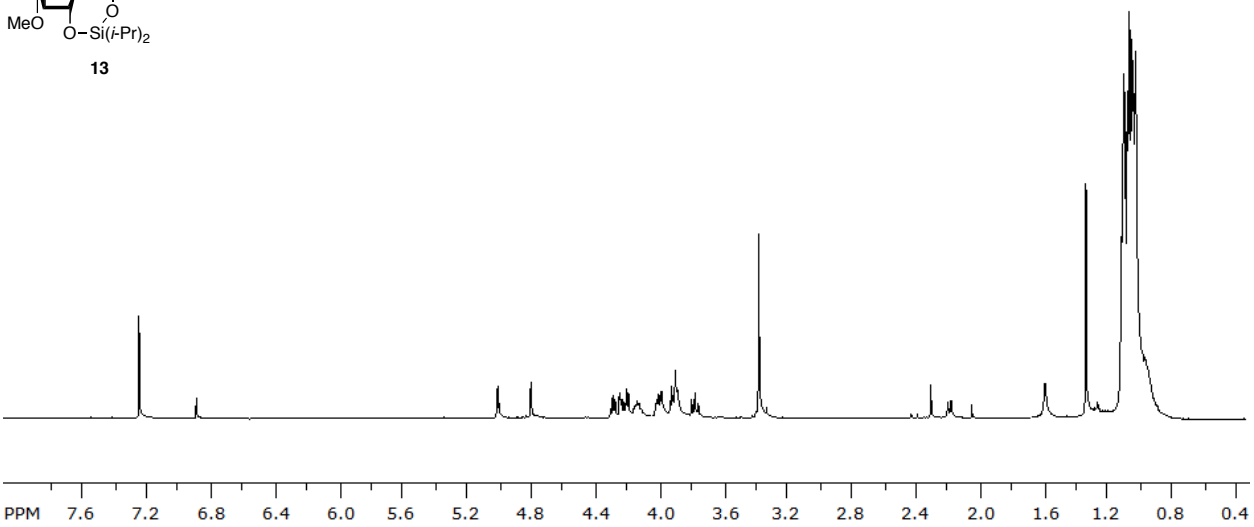


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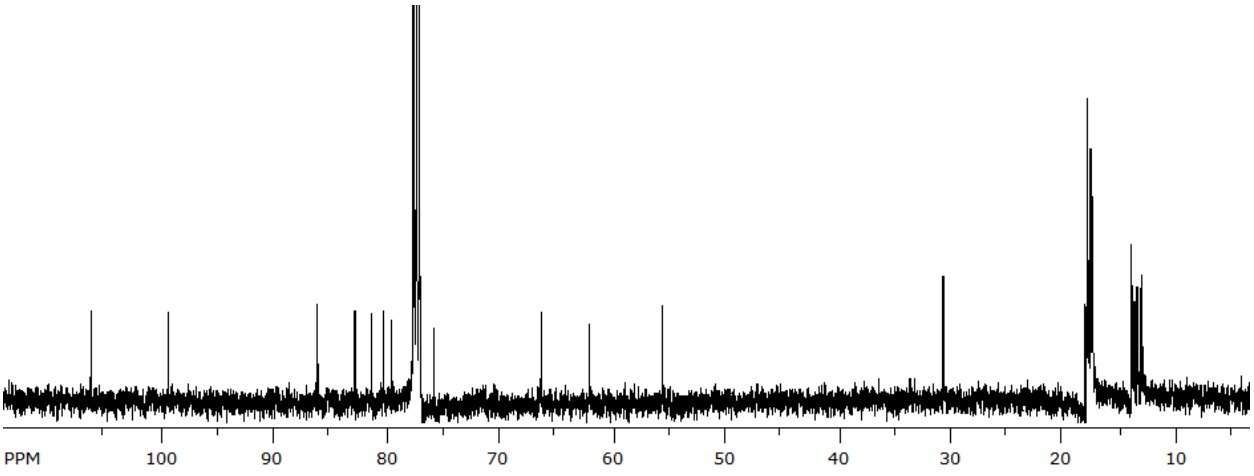

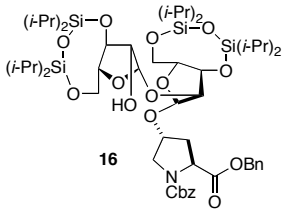


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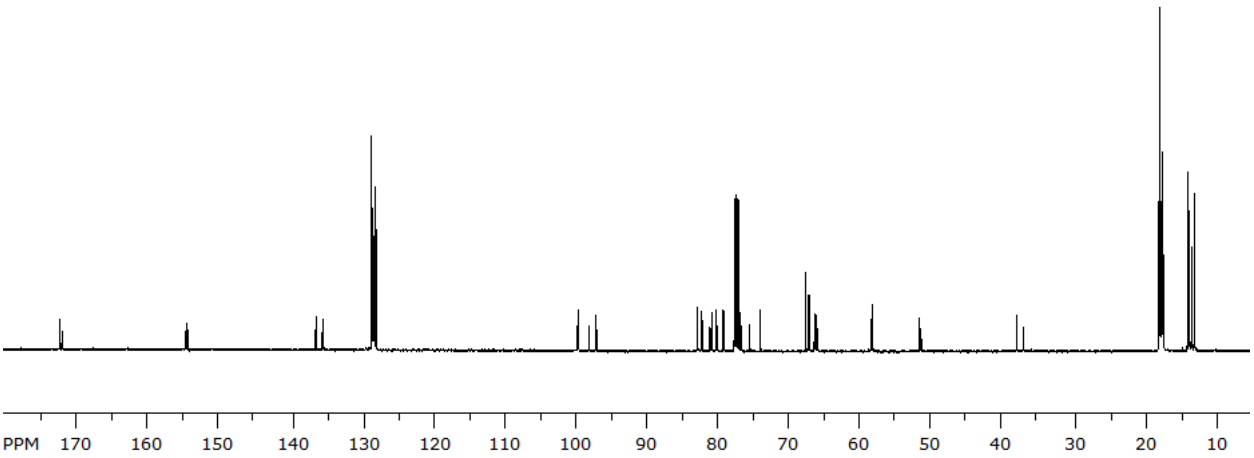
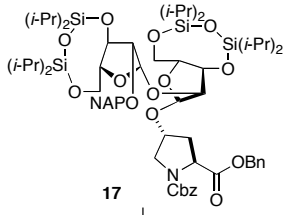
**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



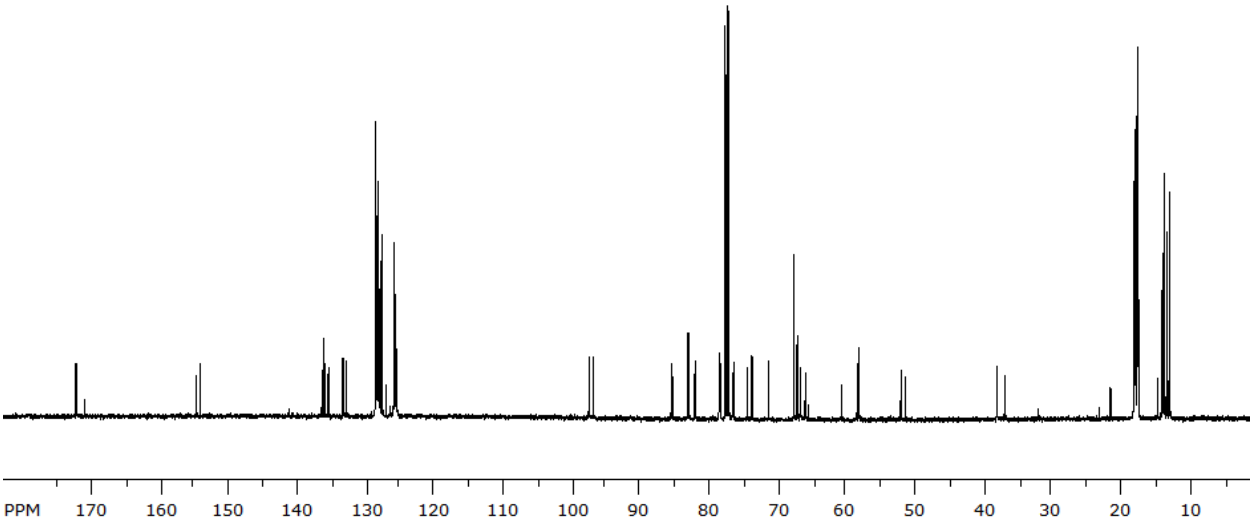


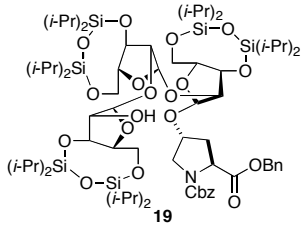

17

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)




**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



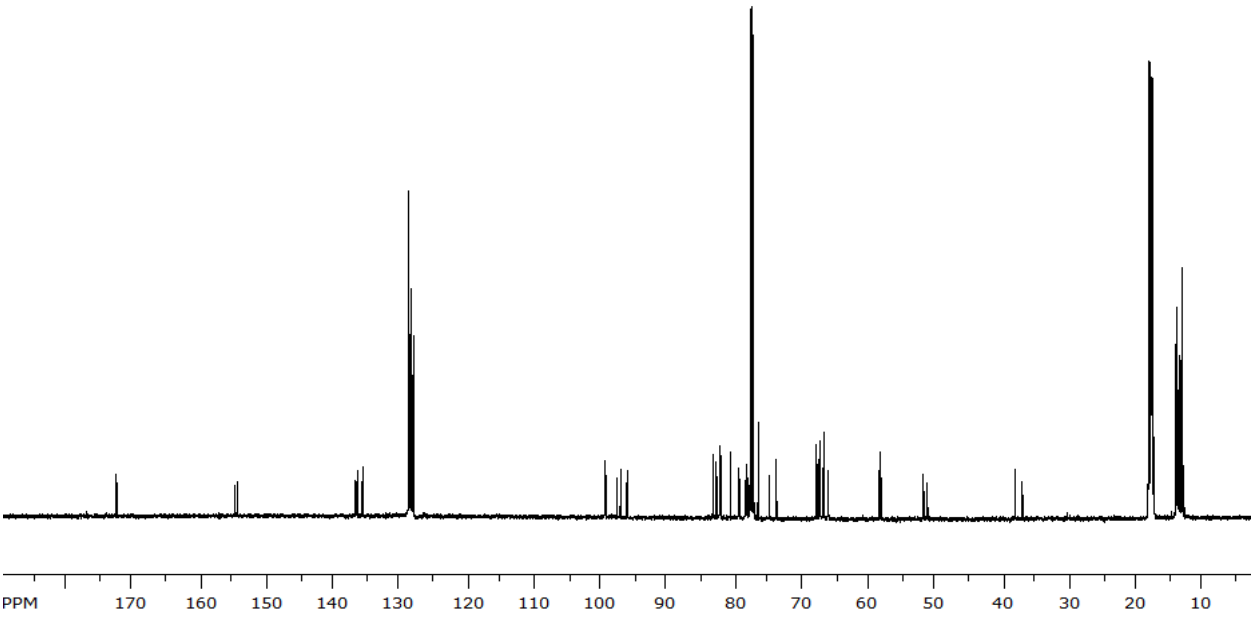


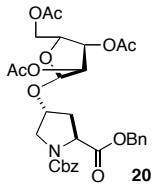

**19**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)




**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



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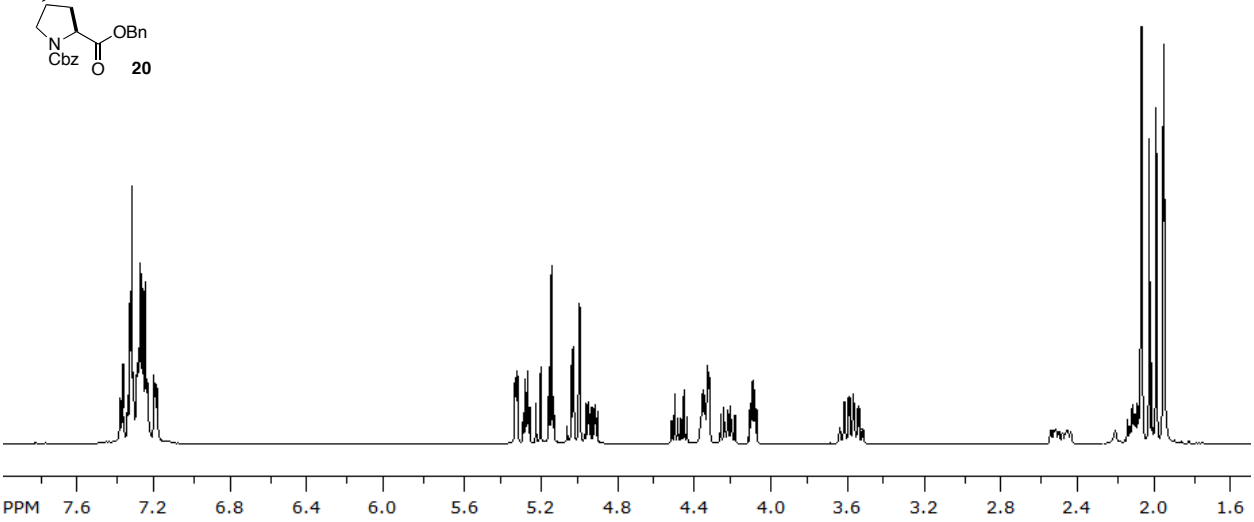


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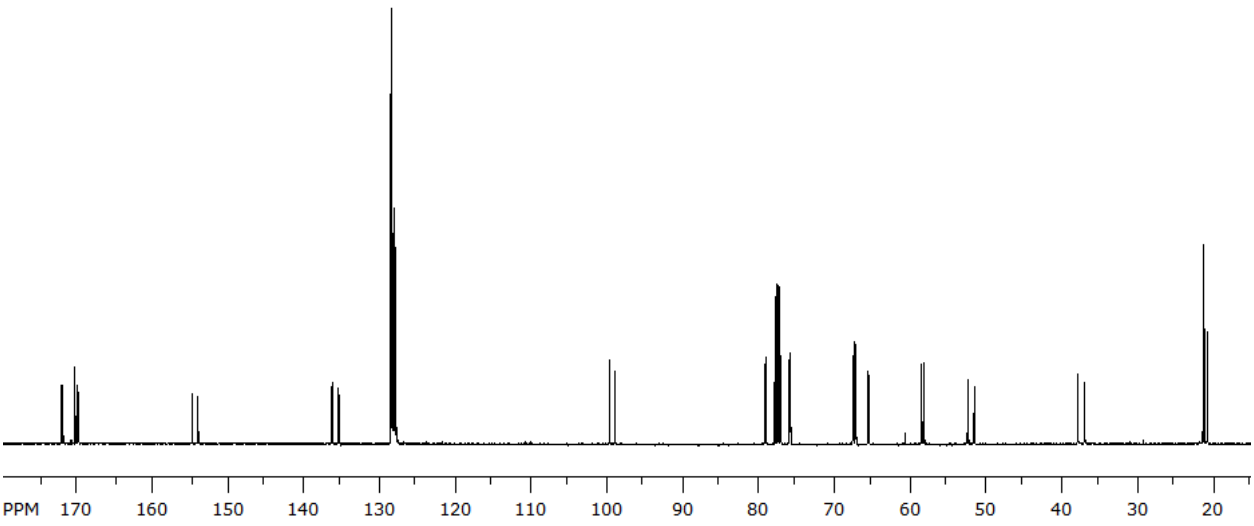
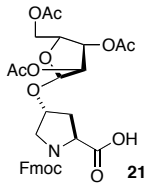


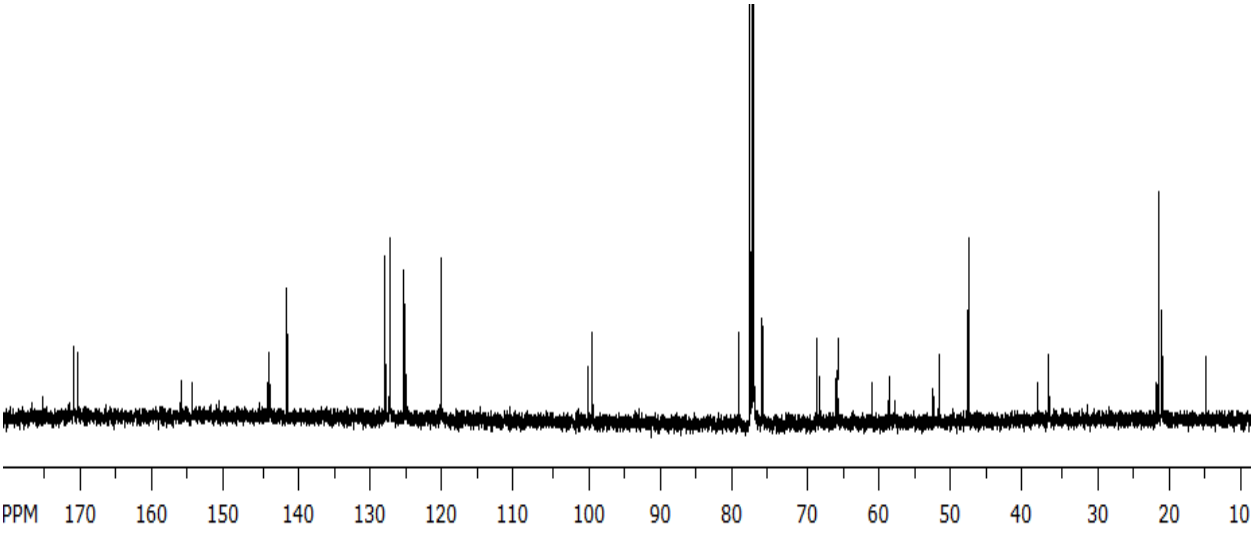


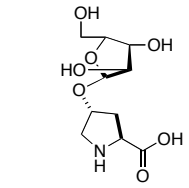

21

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)



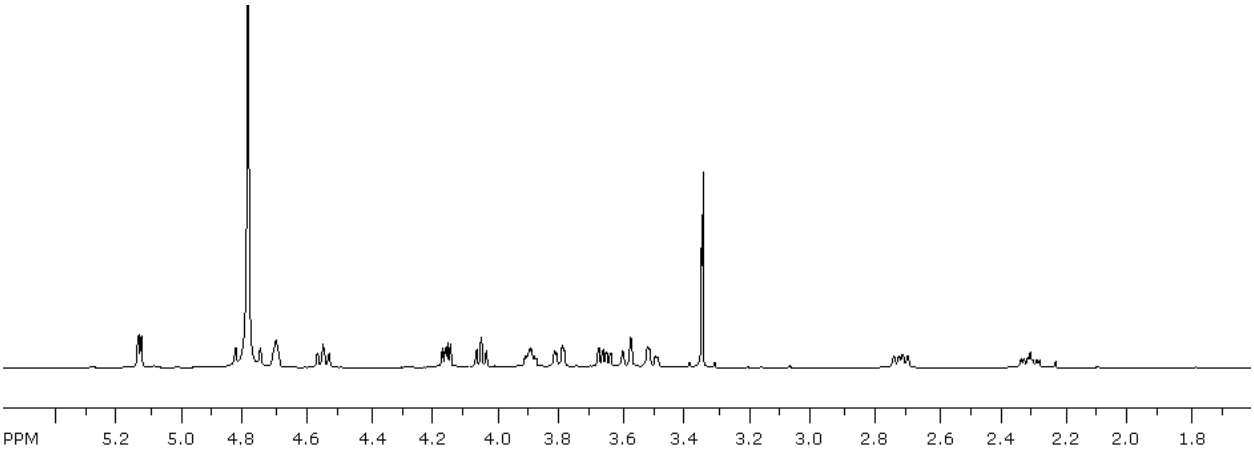

**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



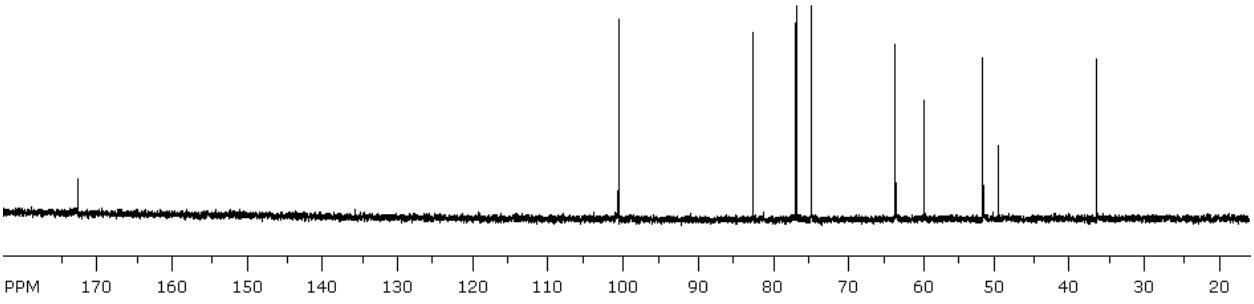


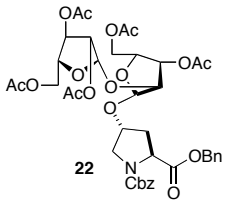

Deprotected compound of **10**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)



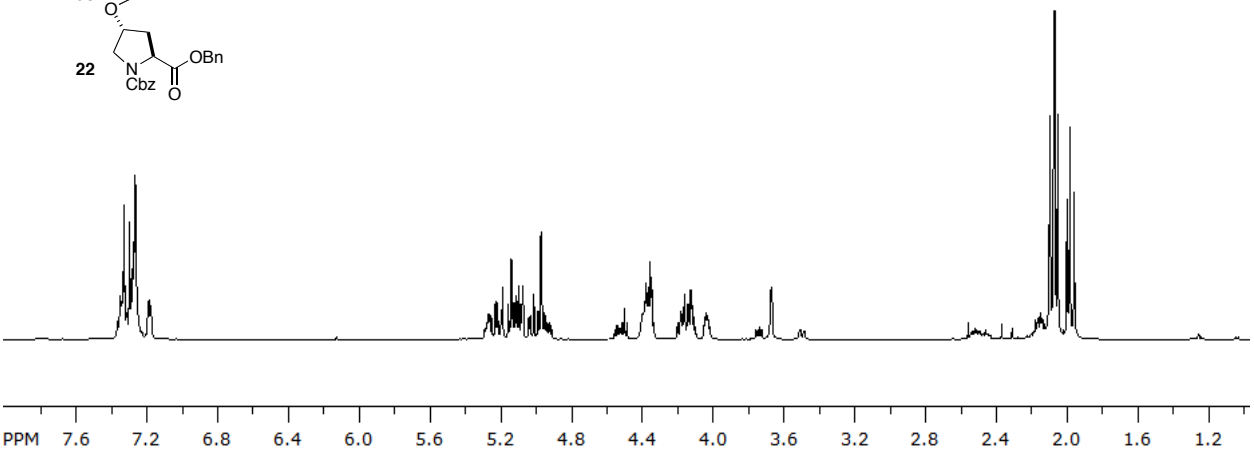

**$^{13}$C NMR** ($CDCl_3$, 125 MHz)






**22**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)

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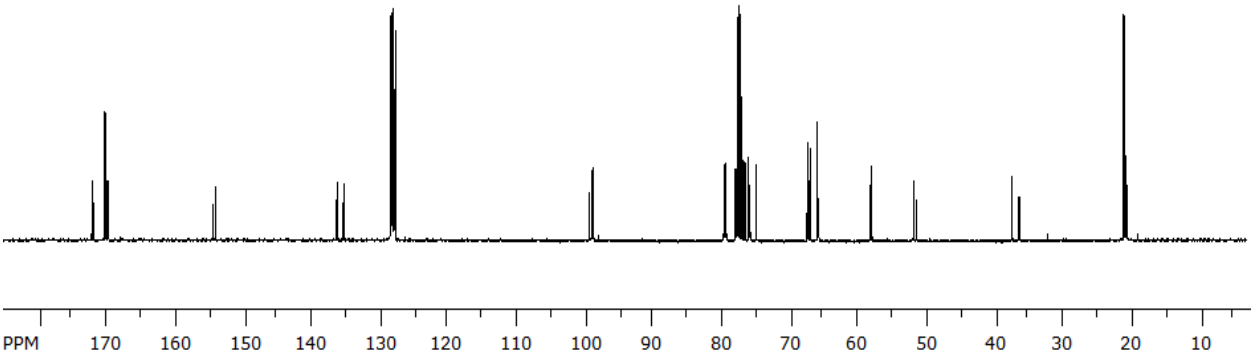

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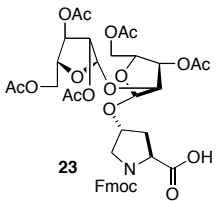


**23**




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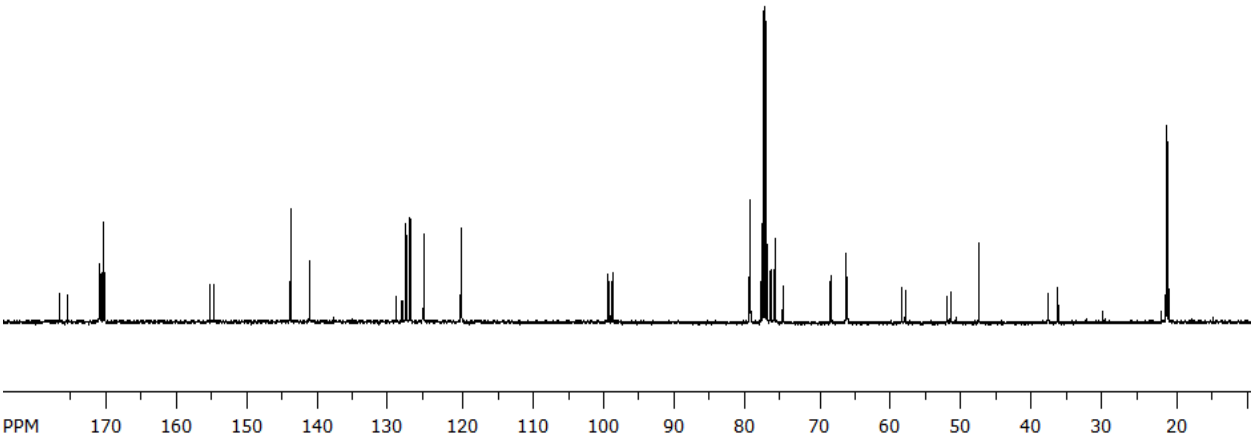

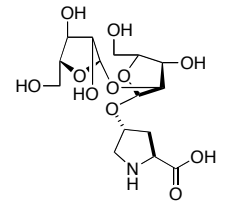


Deprotected compound of **16**

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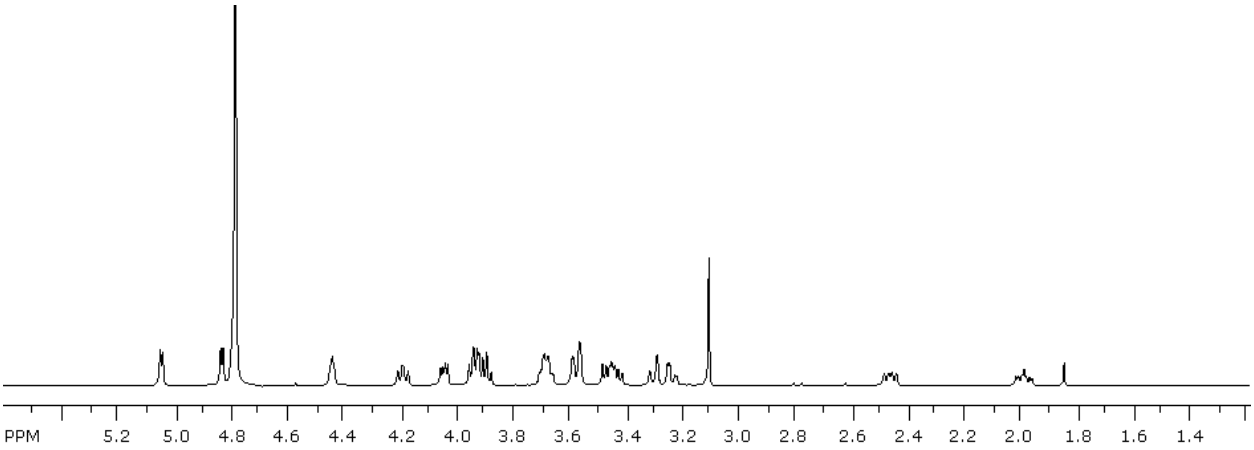
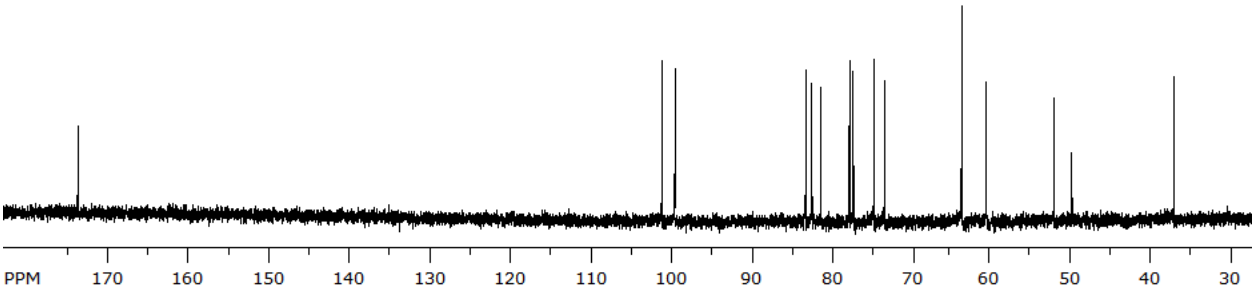
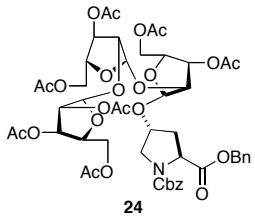


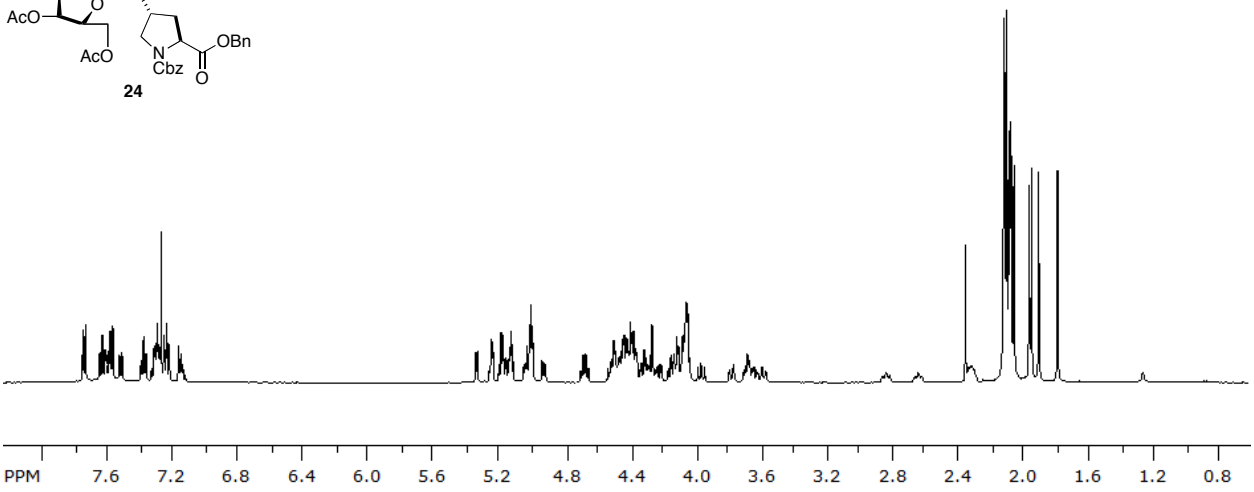

**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



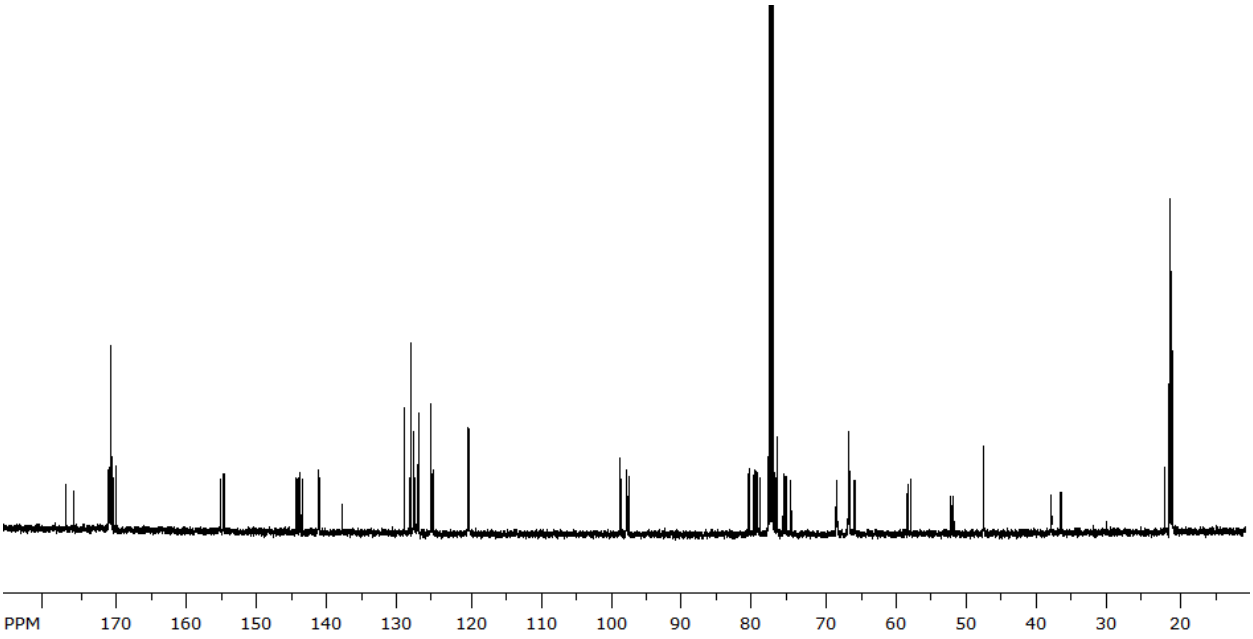


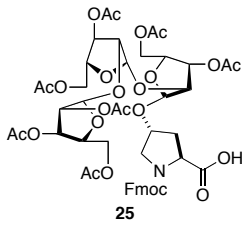

**24**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)



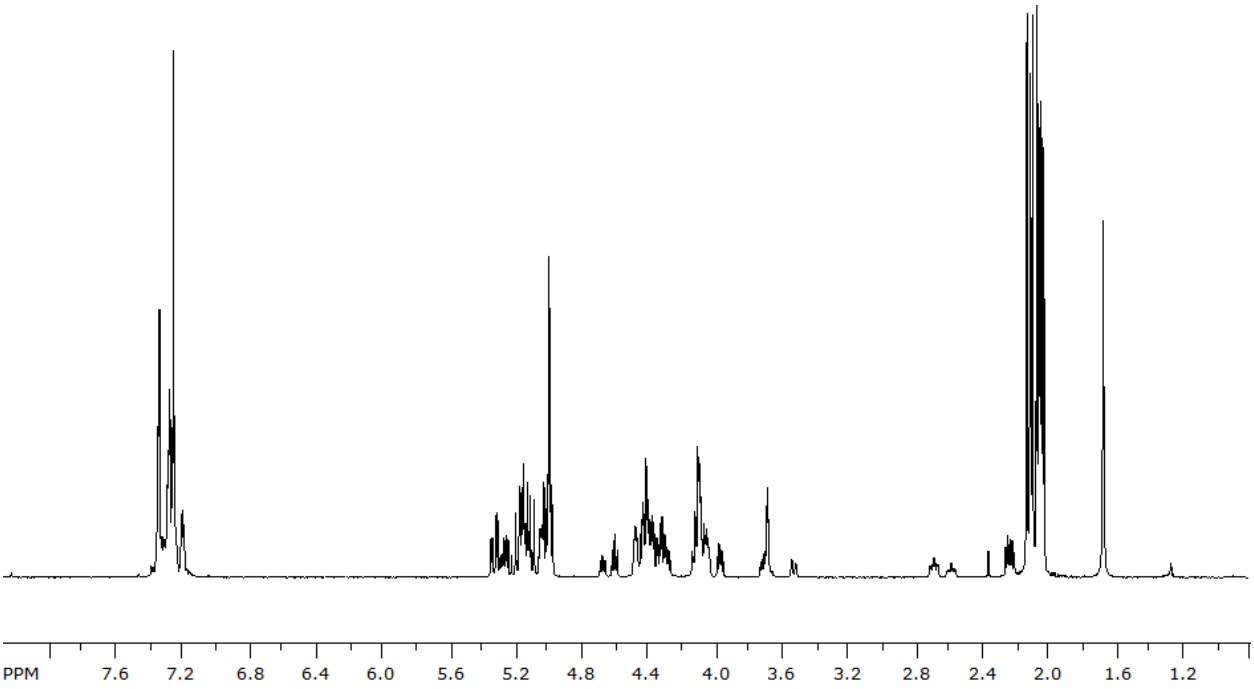

**$^{13}$C NMR** ($CDCl_3$, 125 MHz)



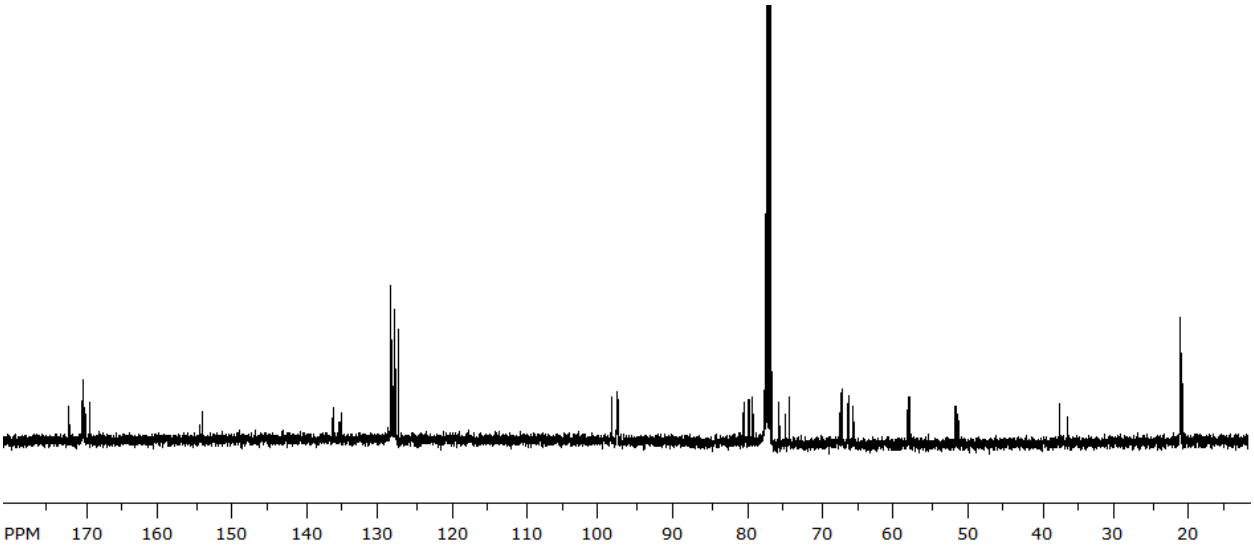


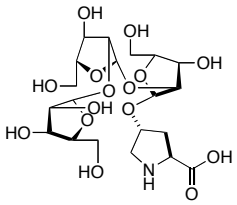

**25**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)



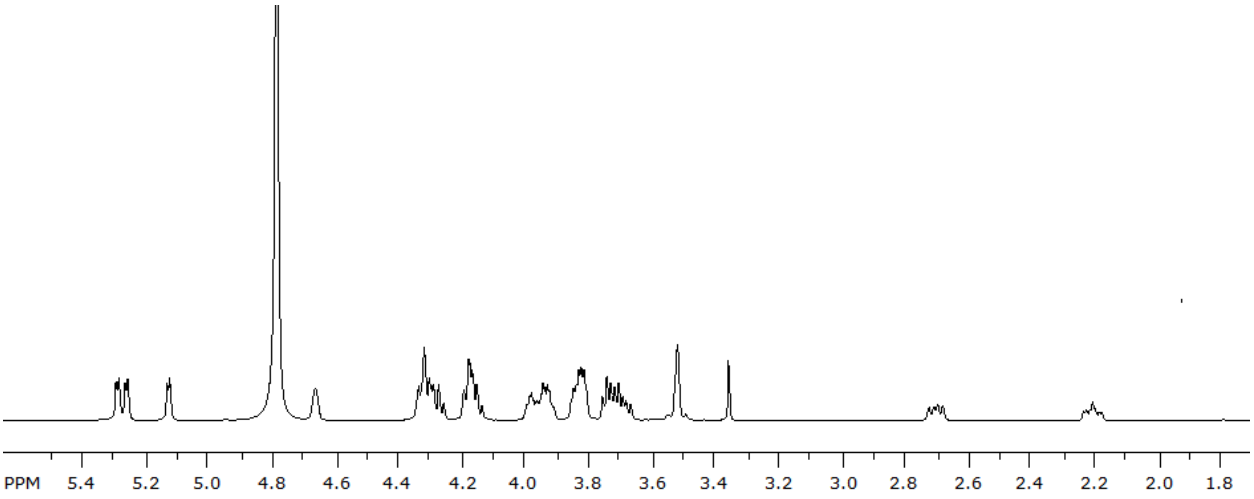

**$^{13}$C NMR** ($CDCl_3$, 125 MHz)






Deprotected compound of **19**

**$^{1}$H NMR** ($CDCl_3$, 500 MHz)

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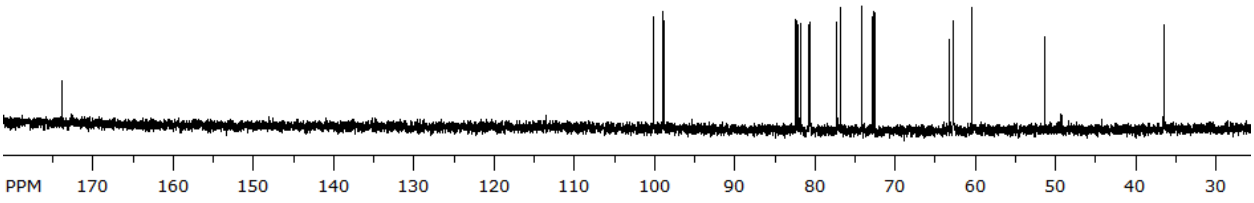
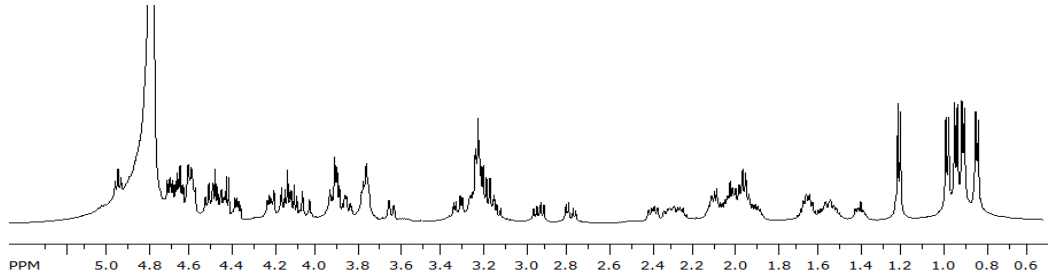
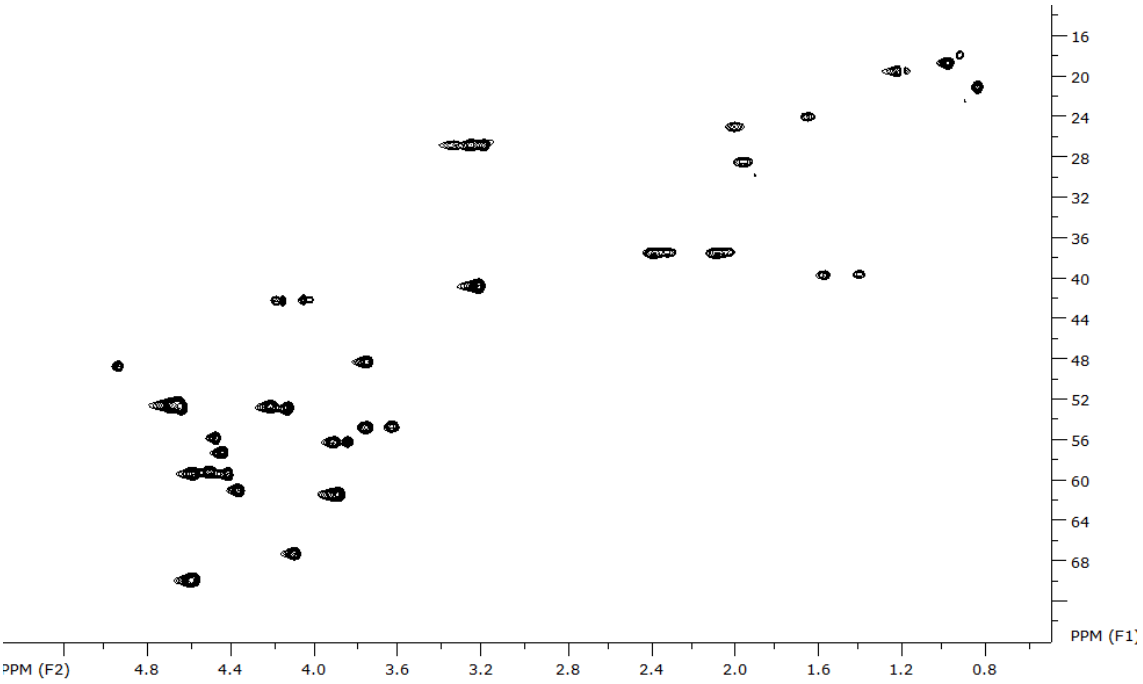


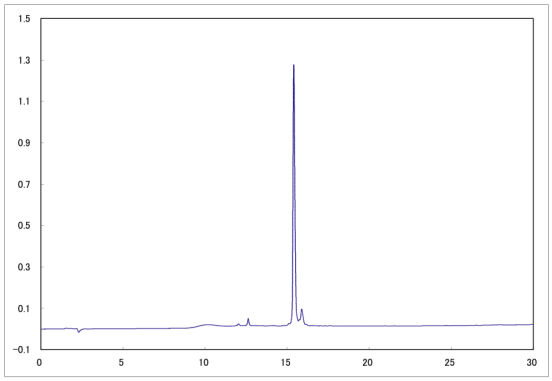
**H-Arg-Thr-Val-Hyp-Ser-Gly-Hyp-Asp-Pro-Leu-His-His-His-OH (4)**

$^{1}$**H NMR** and **HSQC** spectra ($D_2O$, 500 MHz)



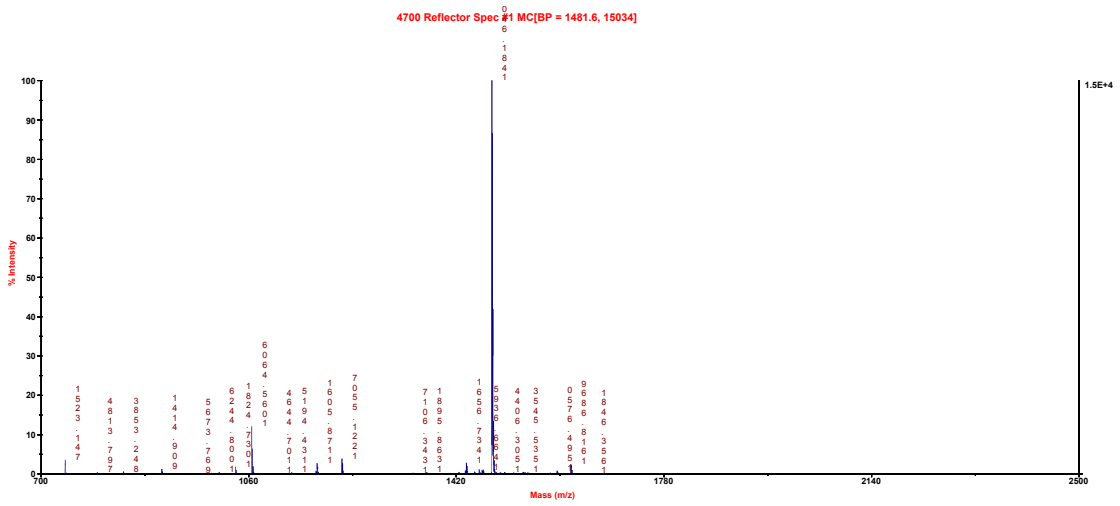




HPLC Chart of **4**

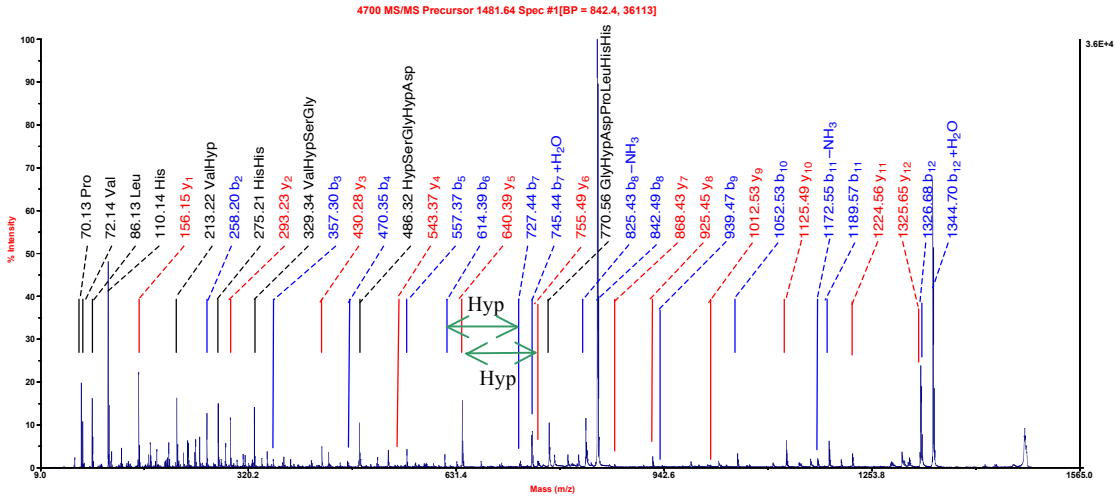


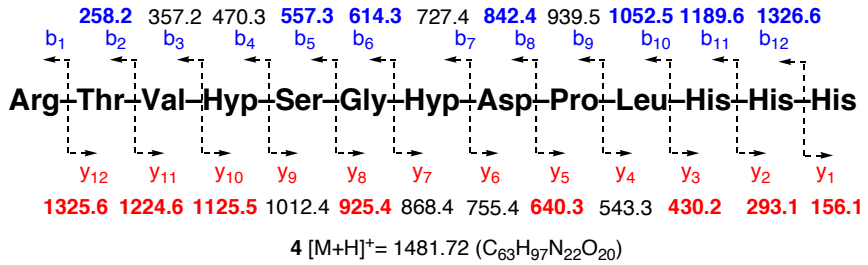

Column : InertSustain C18 (3.0x150)
Eluent: 0.1% TFA $H_2O$–$CH_3CN$
Gradient: 5–5–50–50%/(0–5–35–50 min)
Flow Rate: 0.5 mL/min
Detection: PDA at 220 nm
Retention time: **15.40 min**

Mass spectrum of **4**




Tandem mass spectrum for the ion at *m/z* **1482**



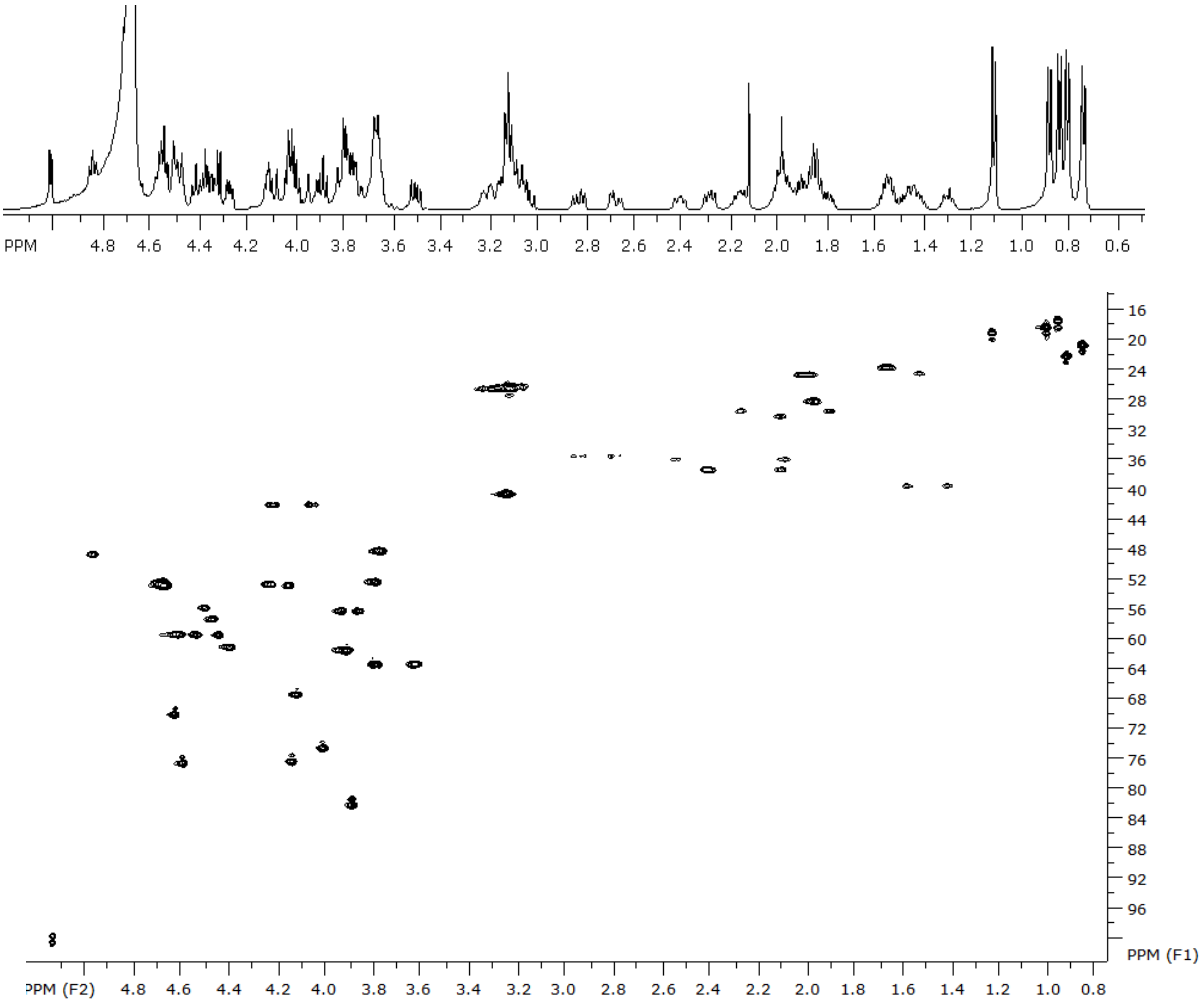




**4** $[M+H]^+$= 1481.72 ($C_{63}H_{97}N_{22}O_{20}$)

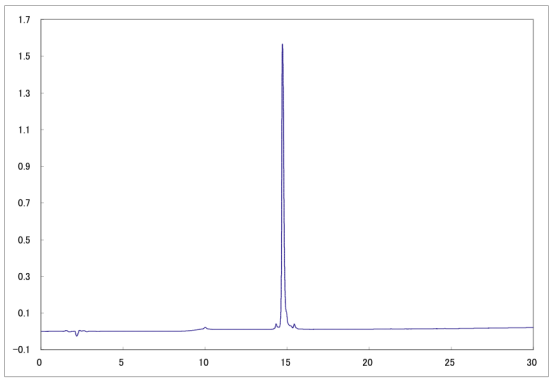
Fragment ions observed by tandem MS/MS analysis of **4**. Numbers upper and lower sides of 13 amino acid sequences are b- (blue) and y- (red) ions, respectively. $b_3$, $b_4$, $b_7$, $b_9$, $y_4$, $y_6$, $y_7$ and $y_9$ ions were also detected though at the small intensity.

**H-Arg-Thr-Val-Hyp-Ser-Gly-Hyp[Ara*f*-β-*O*]-Asp-Pro-Leu-His-His-His-OH (3)**

$^{1}$**H NMR** and **HSQC** spectra ($D_2O$, 500 MHz)

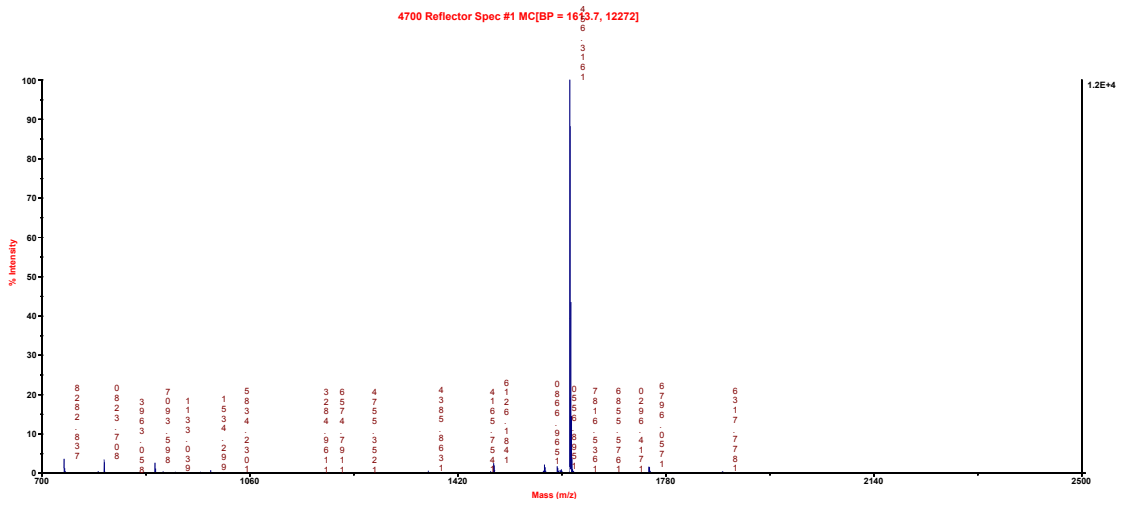



HPLC Chart of **3**

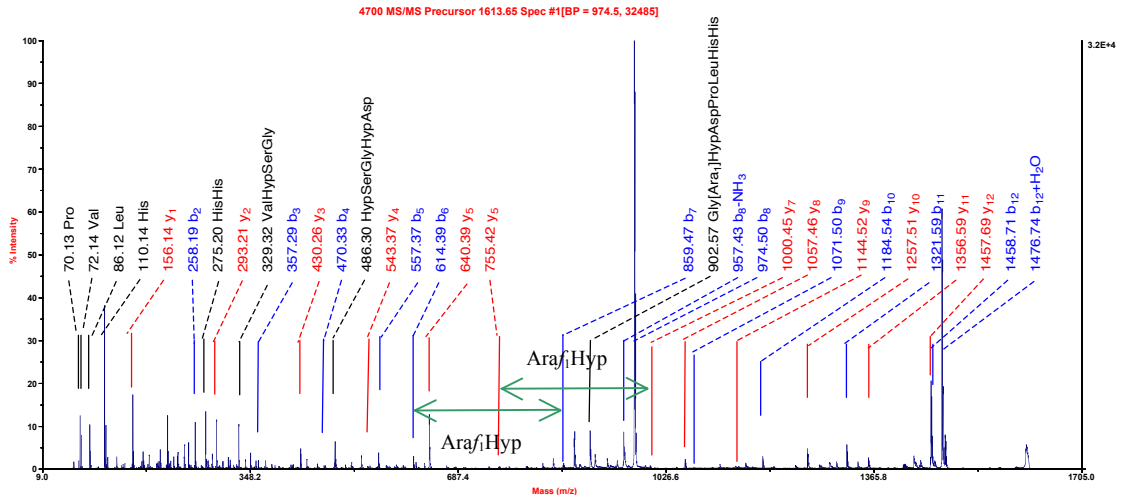


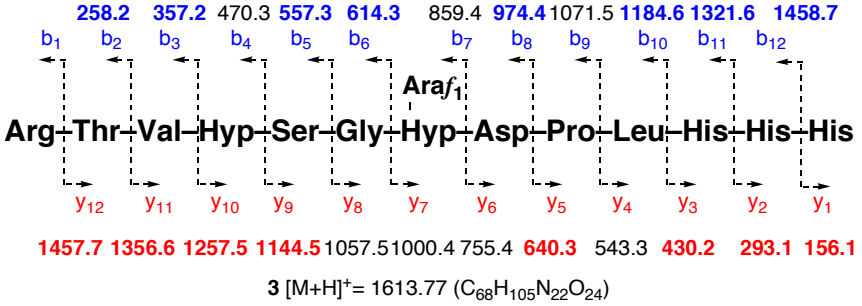

Column : InertSustain C18 (3.0x150)
Eluent: 0.1% TFA $H_2O$–$CH_3CN$
Gradient: 5–5–50–50%/(0–5–35–50 min)
Flow Rate: 0.5 mL/min
Detection: PDA at 220 nm
Retention time: **14.72 min**

Mass spectrum of **3**




Tandem mass spectrum for the ion at *m/z* **1614**



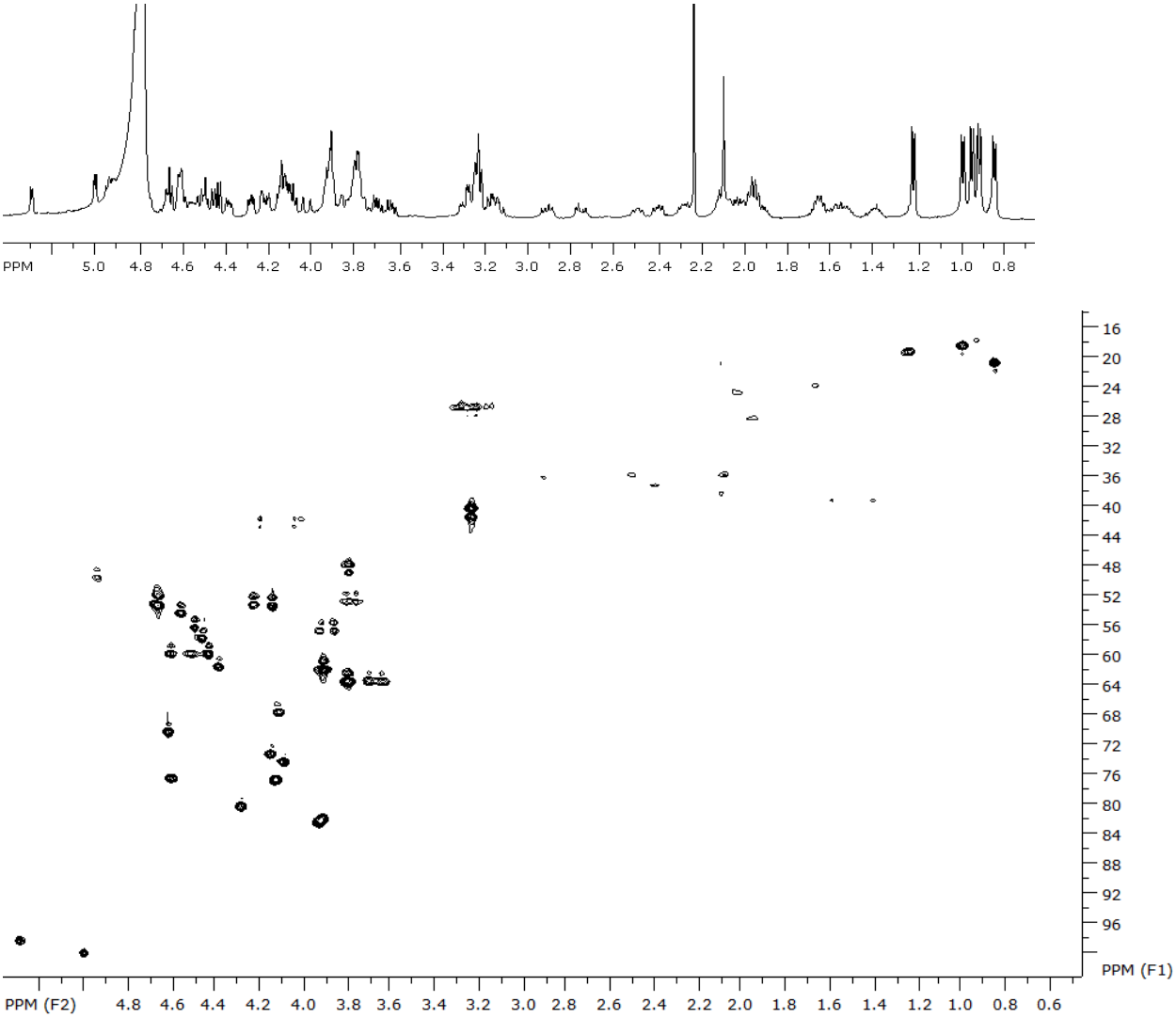




**3** $[M+H]^+$= 1613.77 ($C_{68}H_{105}N_{22}O_{24}$)

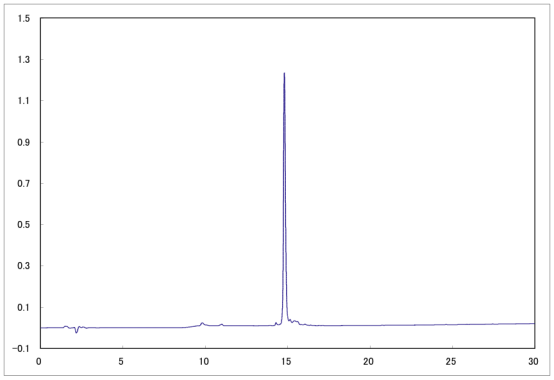
Fragment ions observed by tandem MS/MS analysis of **3**. Numbers upper and lower sides of 13 amino acid sequences are b- (blue) and y- (red) ions, respectively. $b_4$, $b_7$, $b_9$, $y_4$, $y_6$, $y_7$ and $y_8$ ions were also detected though at the small intensity.

**H-Arg-Thr-Val-Hyp-Ser-Gly-Hyp[Ara*f*$_2$-β-*O*]-Asp-Pro-Leu-His-His-His-OH (2)**

$^1$**H NMR** and **HSQC** spectra ($D_2O$, 500 MHz)

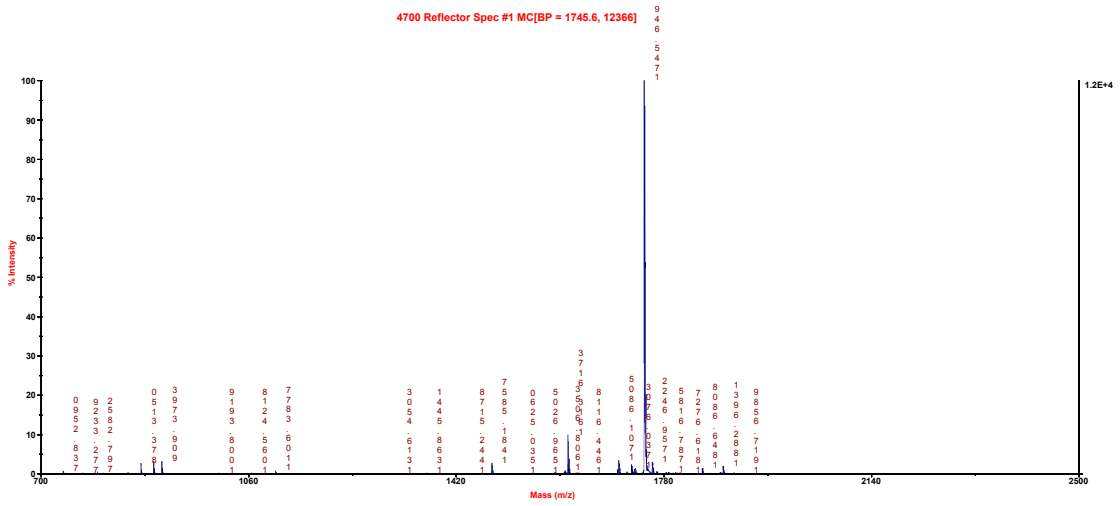



HPLC Chart of **2**

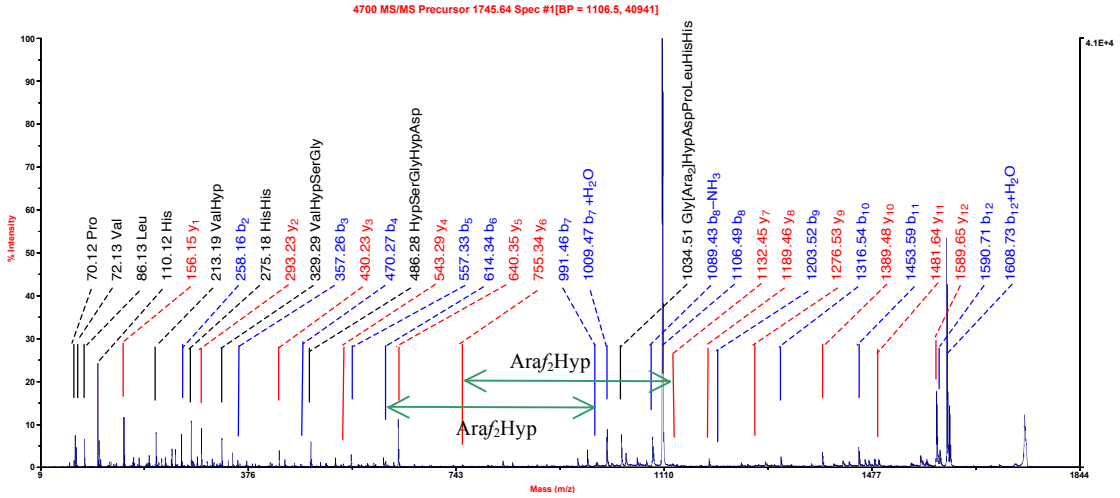


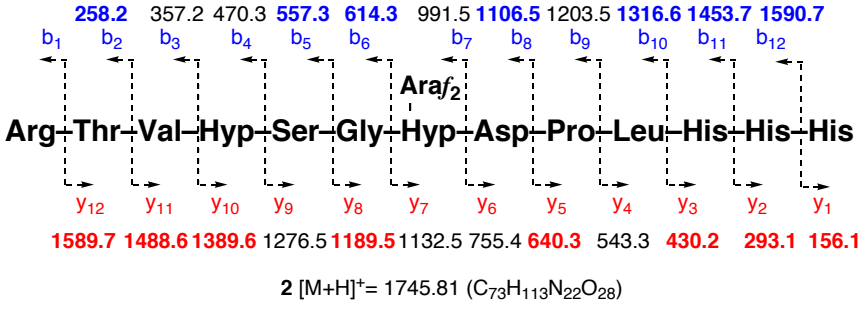

Column : InertSustain C18 (3.0x150)
Eluent: 0.1% TFA $H_2O$–$CH_3CN$
Gradient: 5–5–50–50%/(0–5–35–50 min)
Flow Rate: 0.5 mL/min
Detection: PDA at 220 nm
Retention time: **14.80 min**

Mass spectrum of **2**




Tandem mass spectrum for the ion at *m/z* **1746**



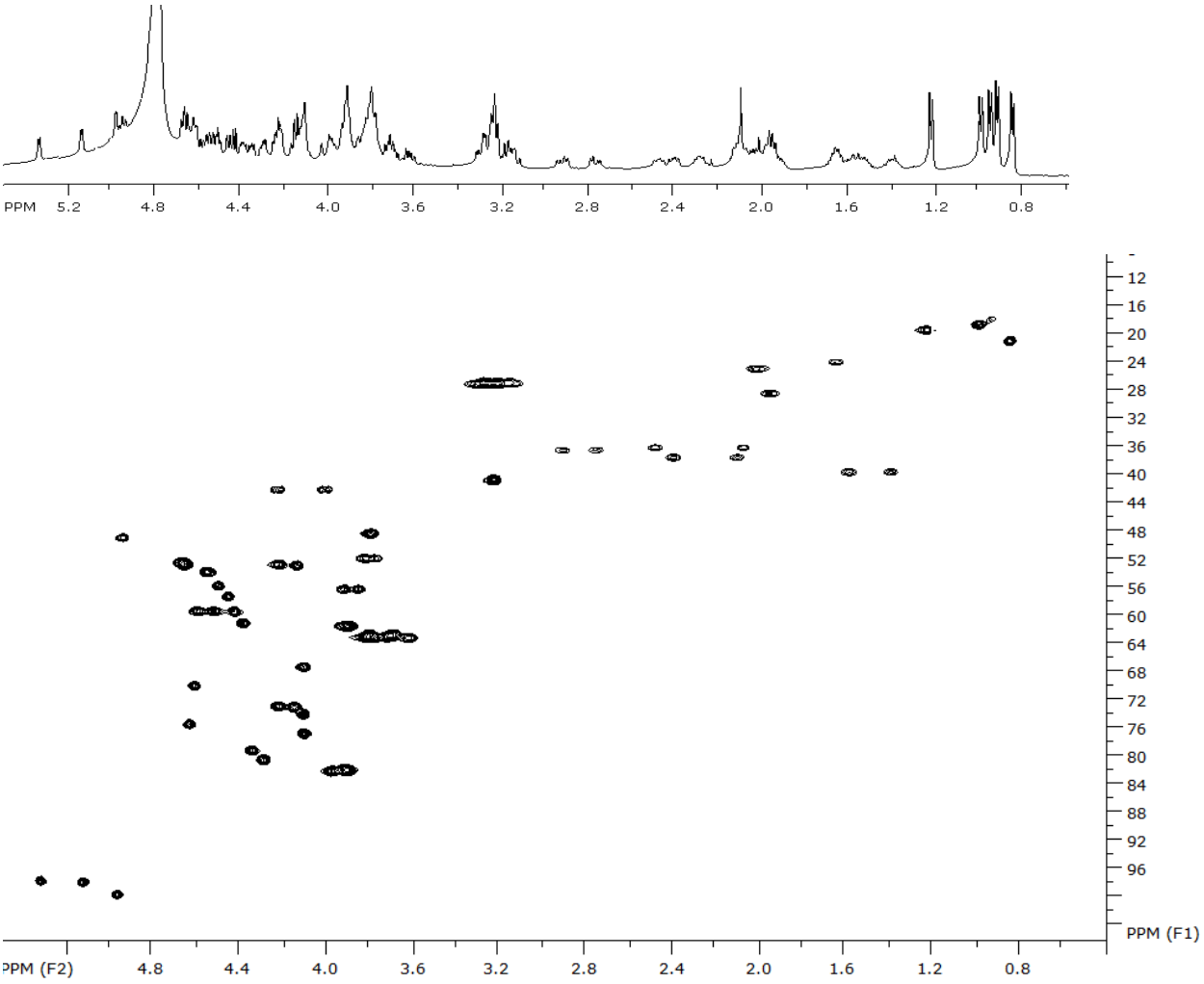




**2** $[M+H]^+$= 1745.81 ($C_{73}H_{113}N_{22}O_{28}$)

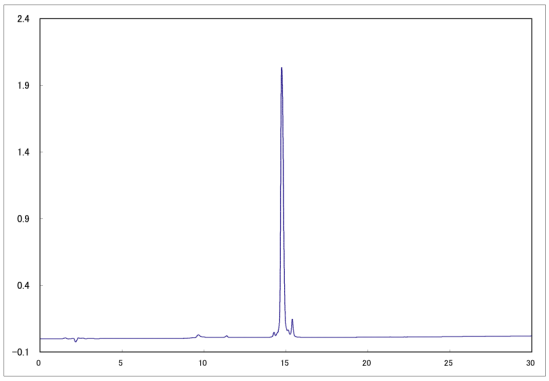
Fragment ions observed by tandem MS/MS analysis of **2**. Numbers upper and lower sides of 13 amino acid sequences are b- (blue) and y- (red) ions, respectively. $b_3$, $b_4$, $b_7$, $b_9$, $y_4$, $y_6$, $y_7$ and $y_9$ ions were also detected though at the small intensity.

**H-Arg-Thr-Val-Hyp-Ser-Gly-Hyp[Ara*f*$_3$-β-*O*]-Asp-Pro-Leu-His-His-His-OH (1)**

$^1$**H NMR** and **HSQC** spectra ($D_2O$, 500 MHz)

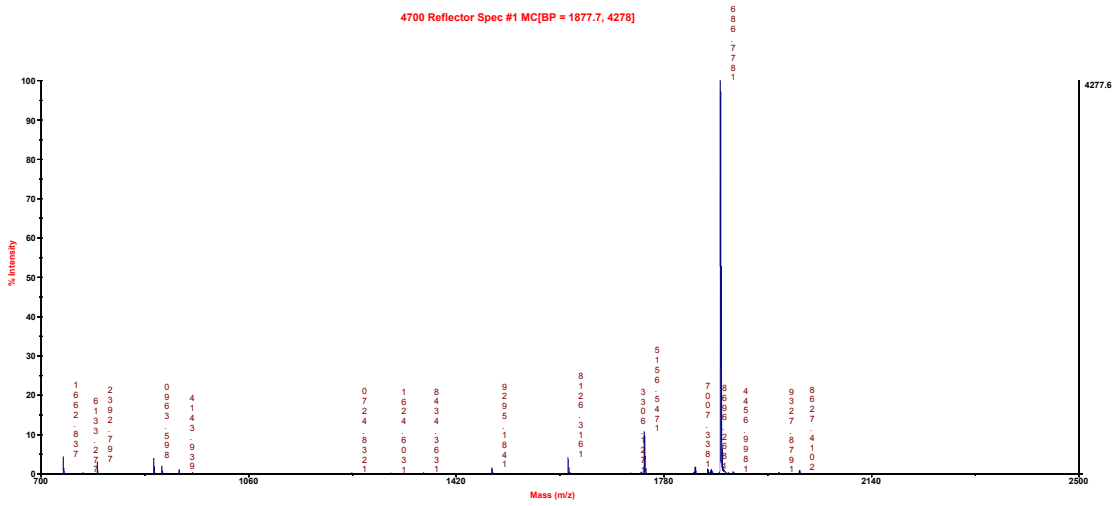



HPLC Chart of **1**

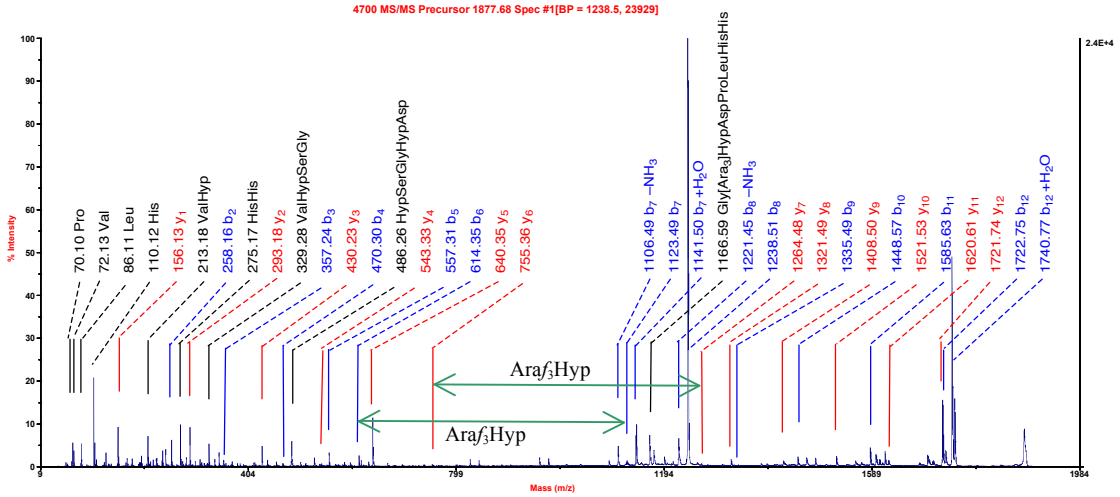


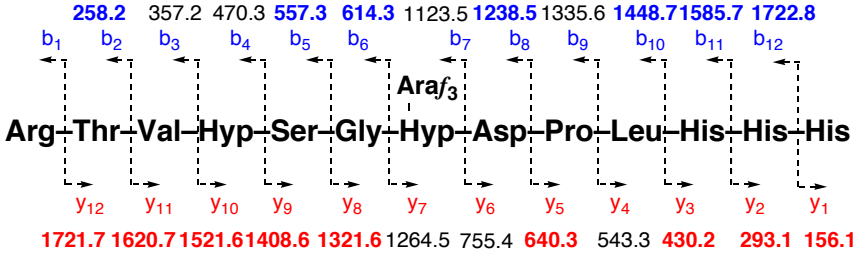

Column : InertSustain C18 (3.0x150)
Eluent: 0.1% TFA $H_2O$–$CH_3CN$
Gradient: 5–5–50–50%/(0–5–35–50 min)
Flow Rate: 0.5 mL/min
Detection: PDA at 220 nm
Retention time: **14.74 min**

Mass spectrum of **1**




Tandem mass spectrum for the ion at *m/z* **1878**




**1** $[M+H]^+$= 1877.85 ($C_{78}H_{121}N_{22}O_{32}$)

Fragment ions observed by tandem MS/MS analysis of **1**. Numbers upper and lower sides of 13 amino acid sequences are b- (blue) and y- (red) ions, respectively. $b_3$, $b_4$, $b_7$, $b_9$, $y_4$, $y_6$ and $y_7$ ions were also detected though at the small intensity.