

## Supplementary Material

### Studies in glycopeptide synthesis

Yasuhiro Kajihara,<sup>a,b\*</sup> Rie Nishikawa,<sup>a</sup> Yuta Maki,<sup>a,b</sup> and Ryo Okamoto<sup>a,b</sup>

<sup>a</sup> Department of Chemistry<sup>1</sup> and Project Research Center for Fundamental Sciences<sup>2</sup>,

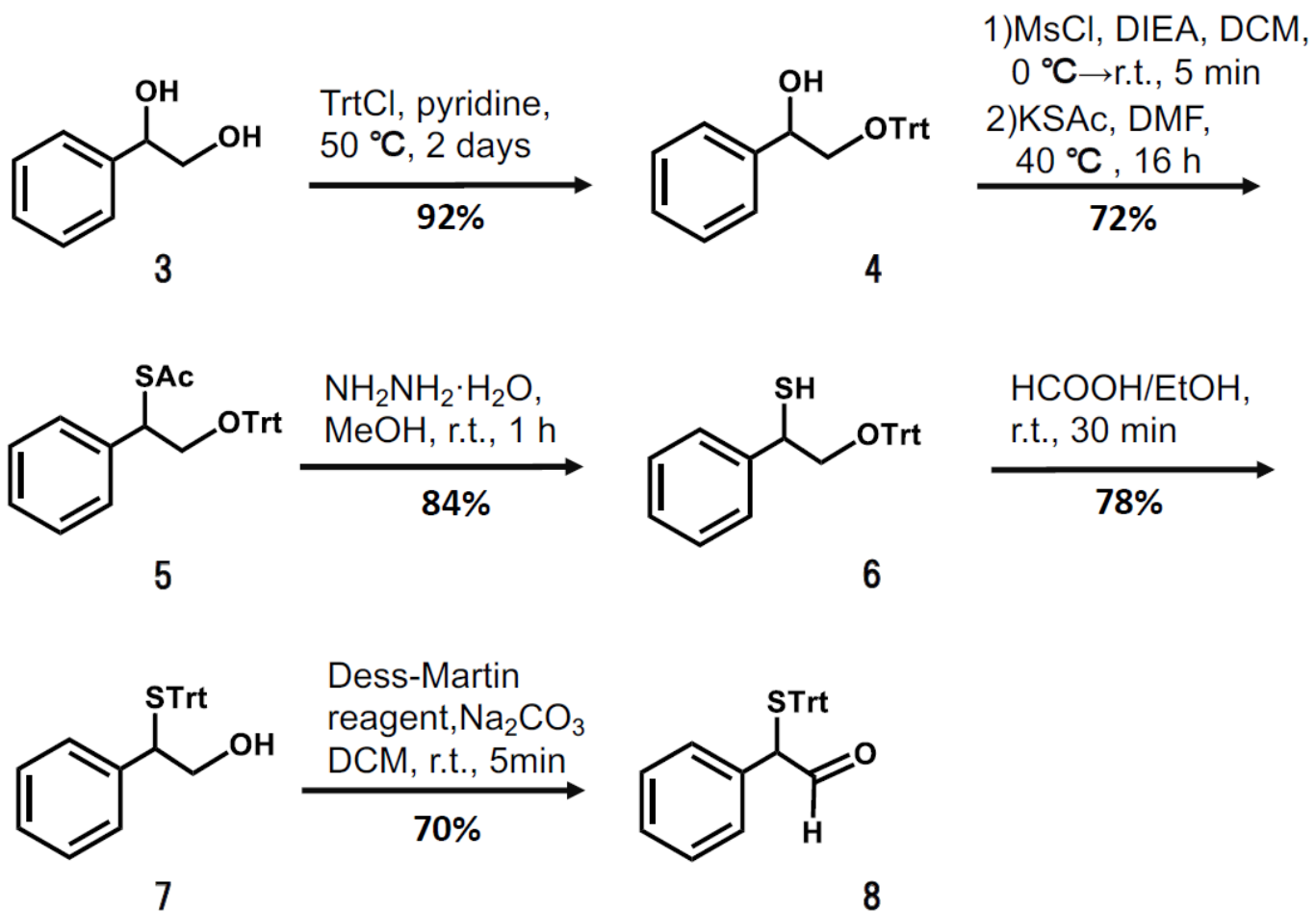
<sup>b</sup> Graduate School of Science, Osaka University, 1-1, Machikaneyama, Toyonaka, 560-0043 Japan

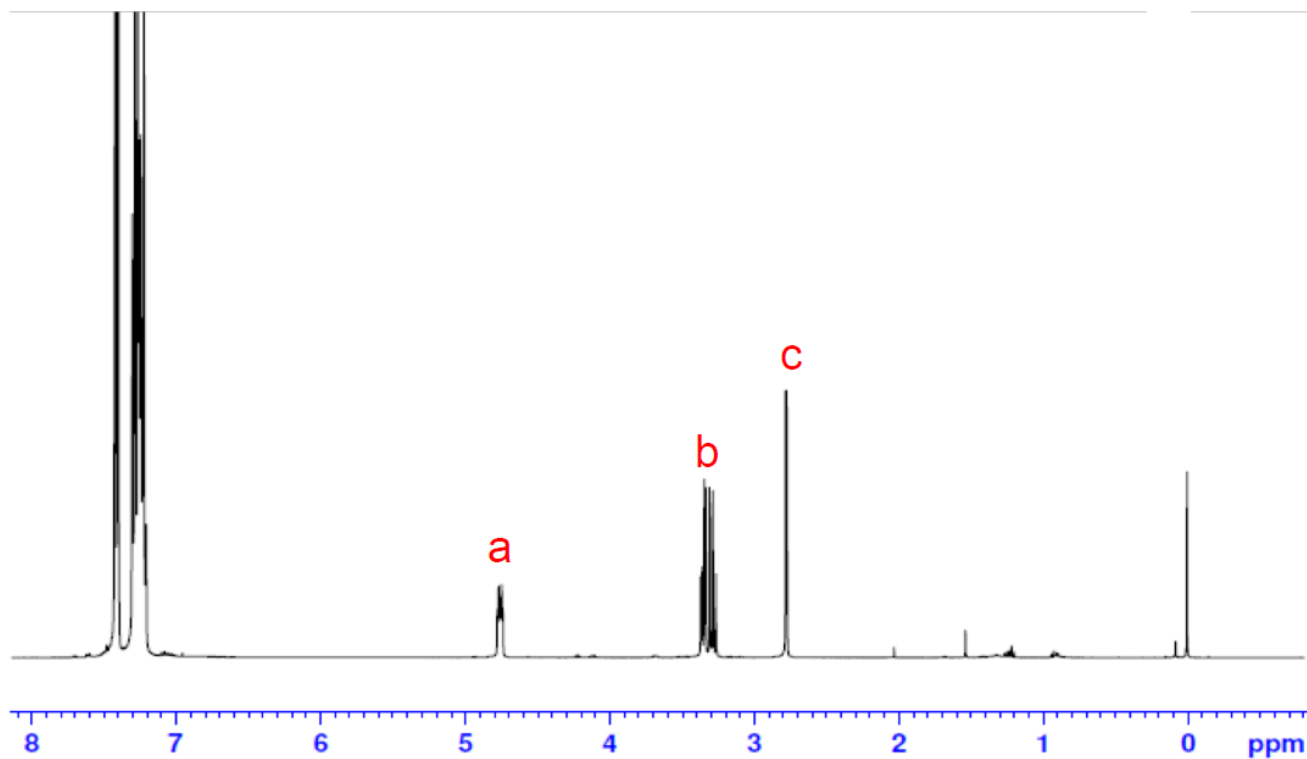
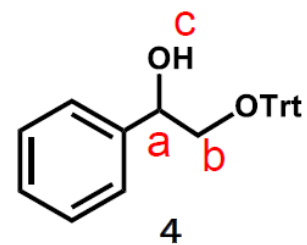
E-mail: [kajihara@chem.sci.osaka-u.ac.jp](mailto:kajihara@chem.sci.osaka-u.ac.jp)

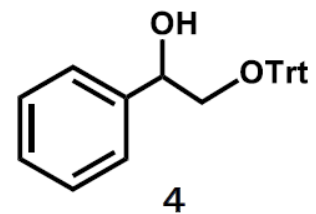
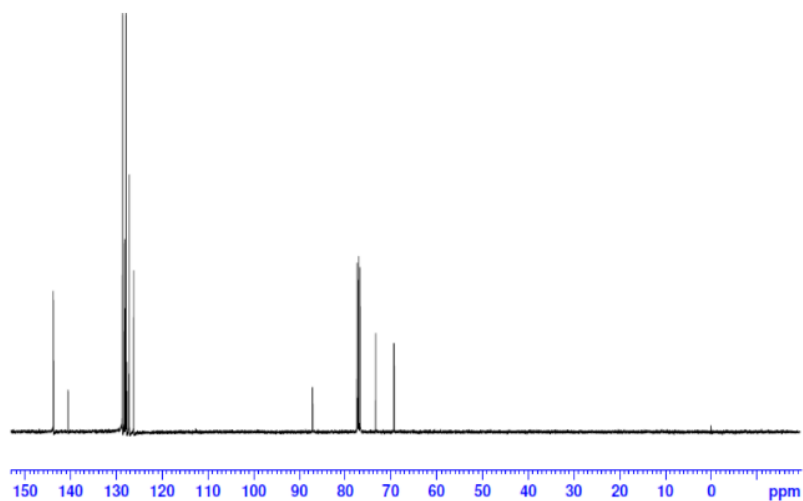
#### Table of Contents

<sup>1</sup> H, <sup>13</sup> C NMR spectra, Mass data, and HPLC profiles of compounds.....	S2
---	----

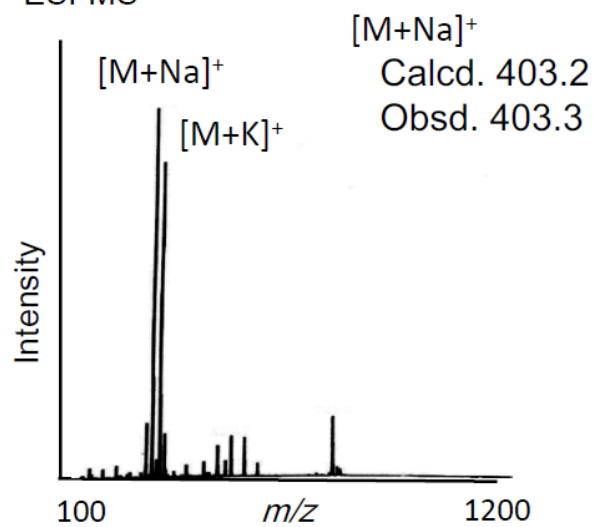
## Synthesis of Auxiliary group

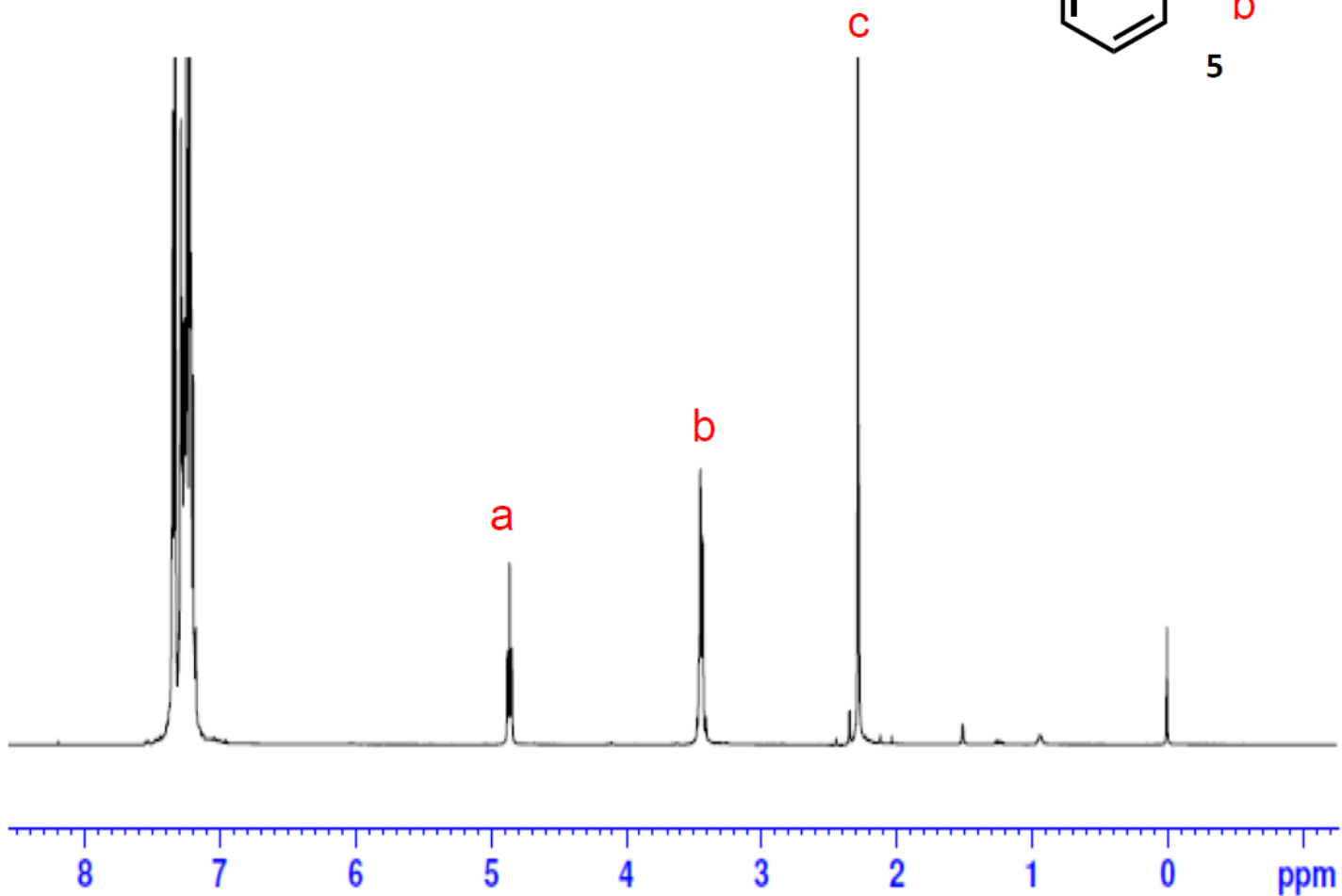
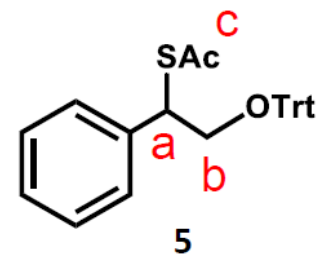


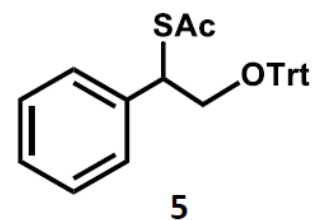
$^1\text{H}$ NMR

 $^{13}\text{C}$ NMR

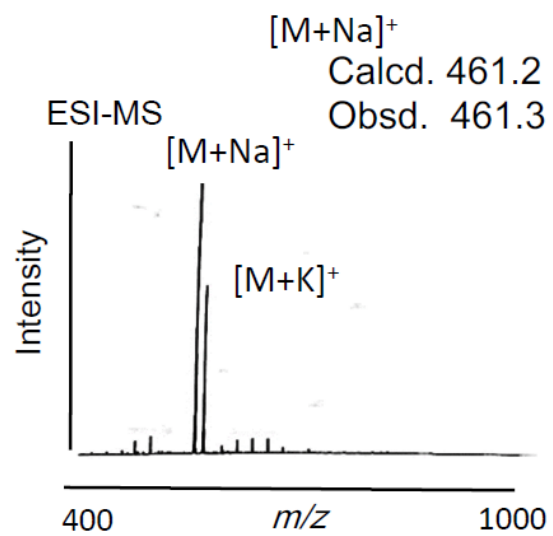
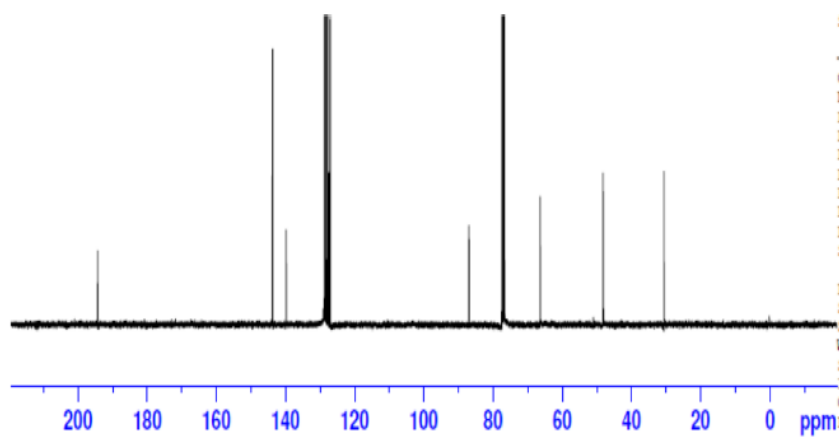
## ESI-MS

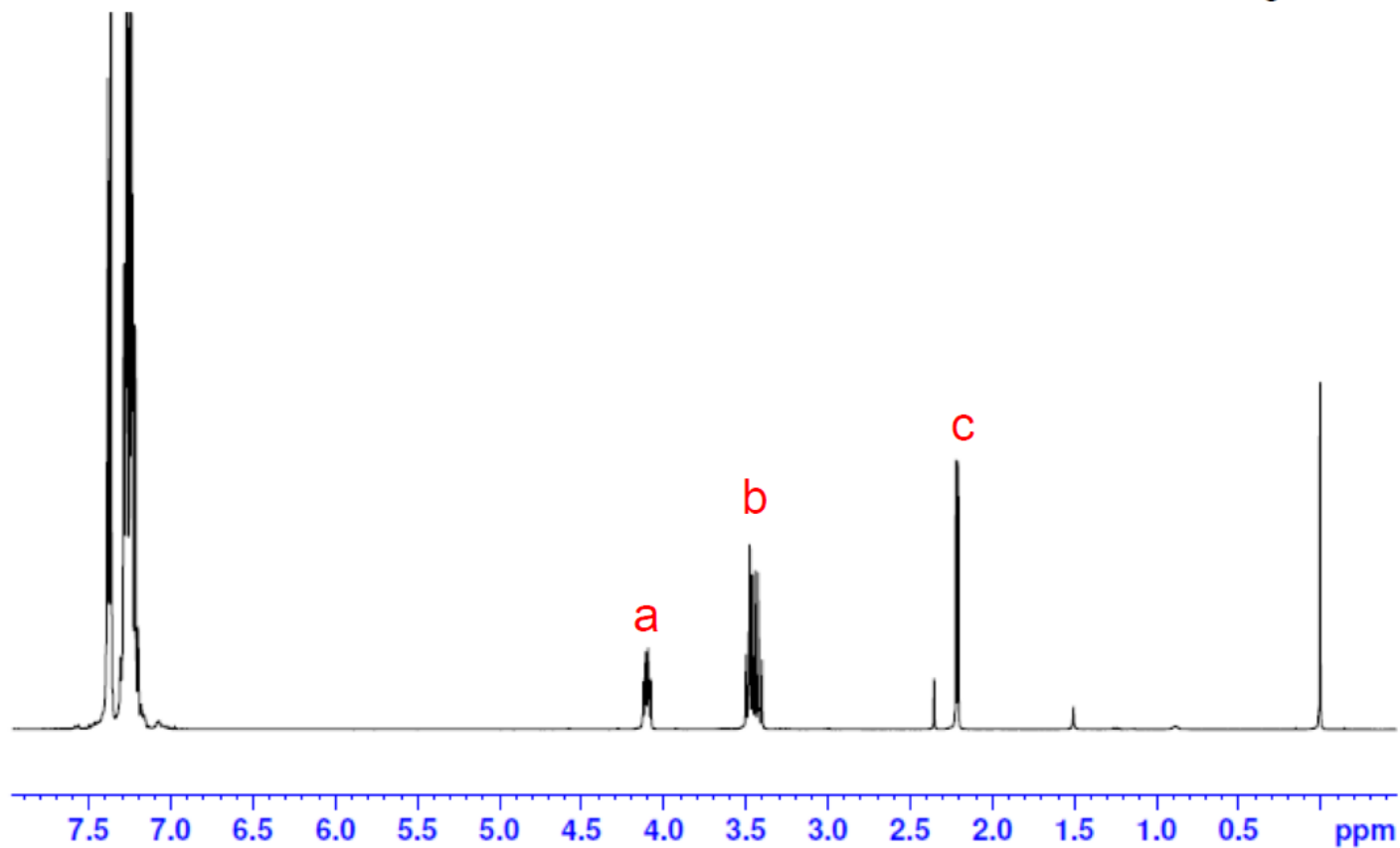
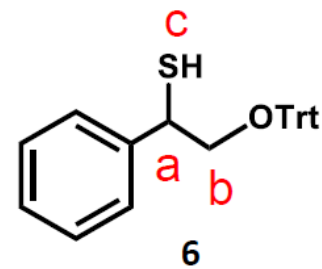


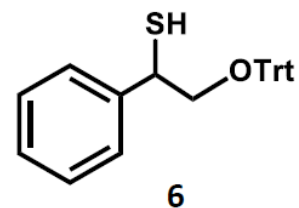
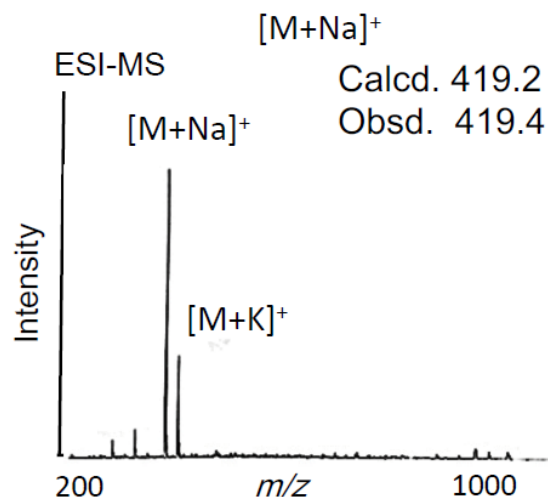
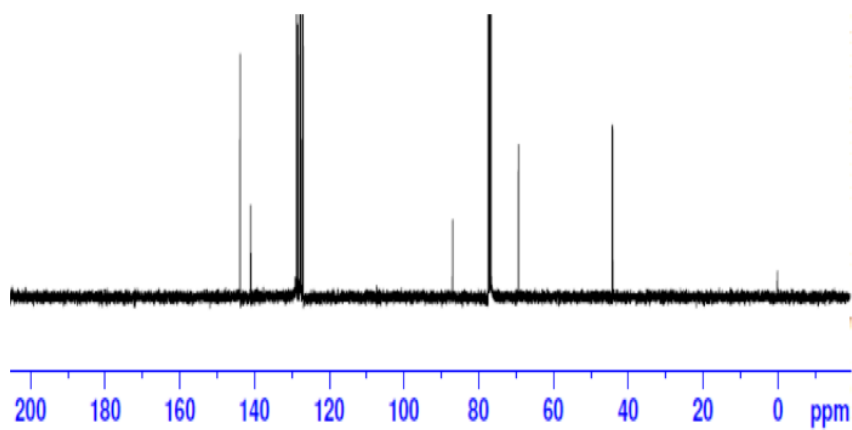
$^1\text{H}$ NMR



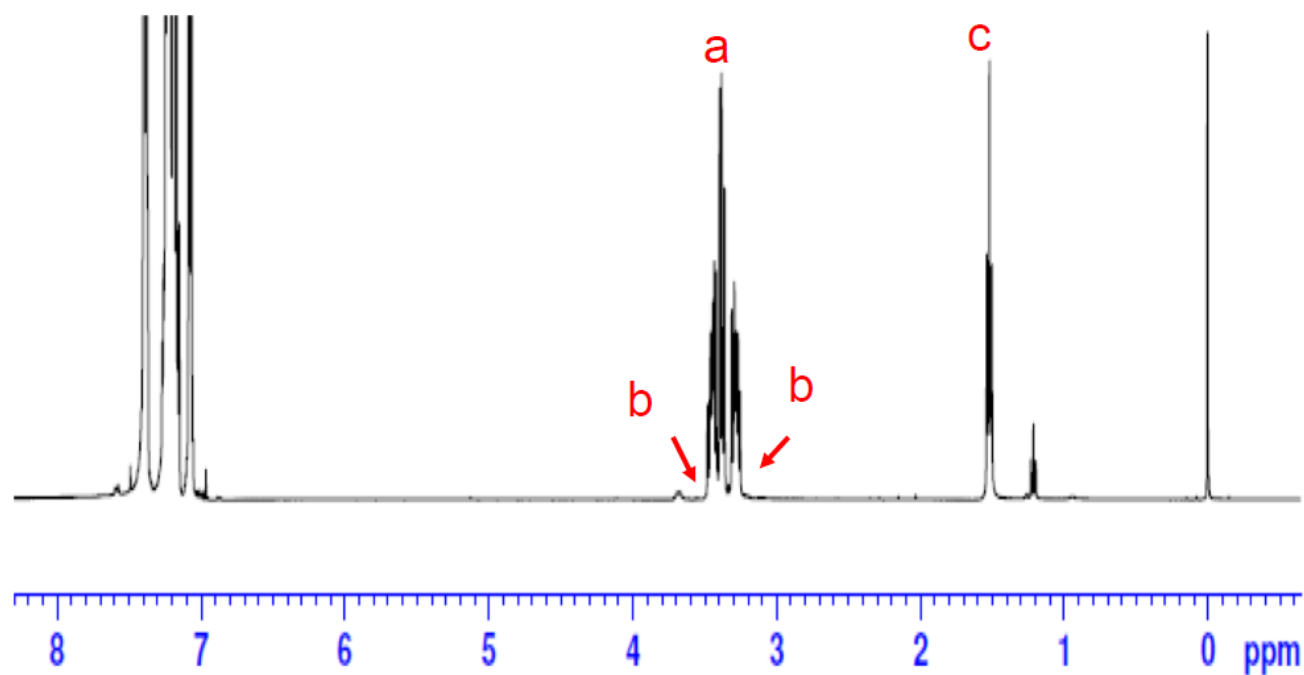
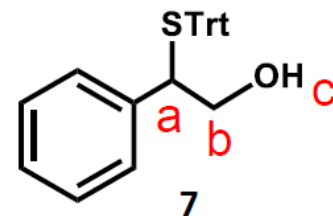
$^{13}\text{C}$ NMR

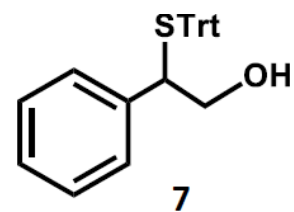
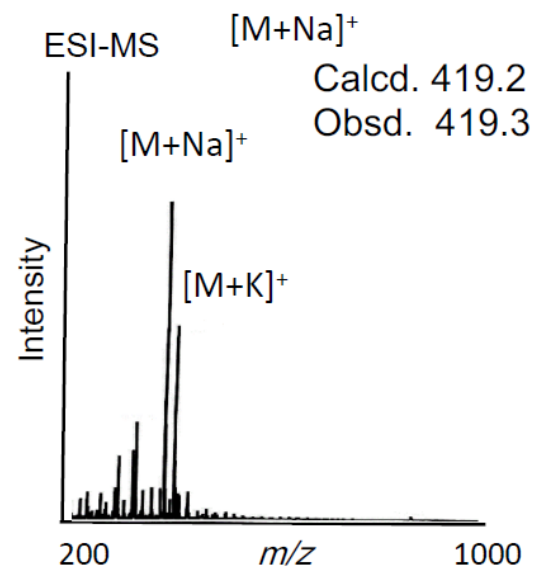
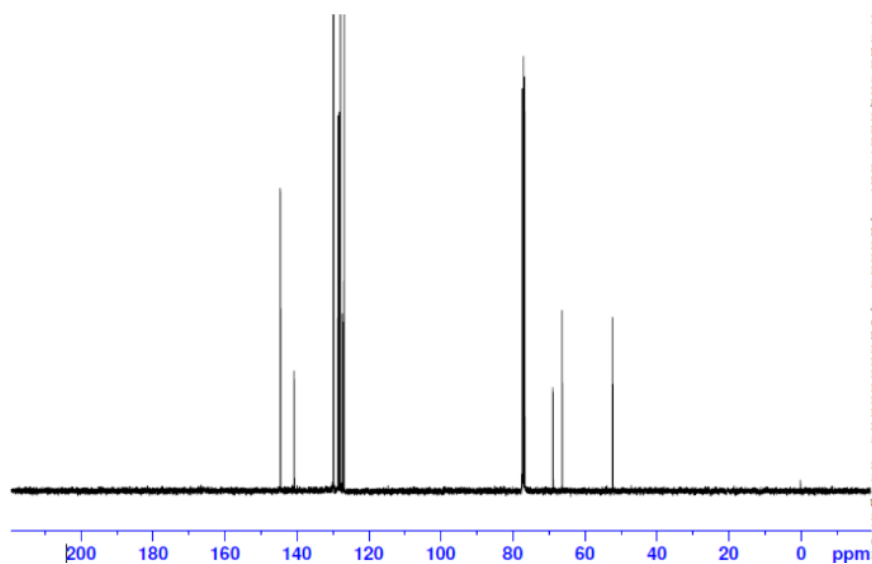


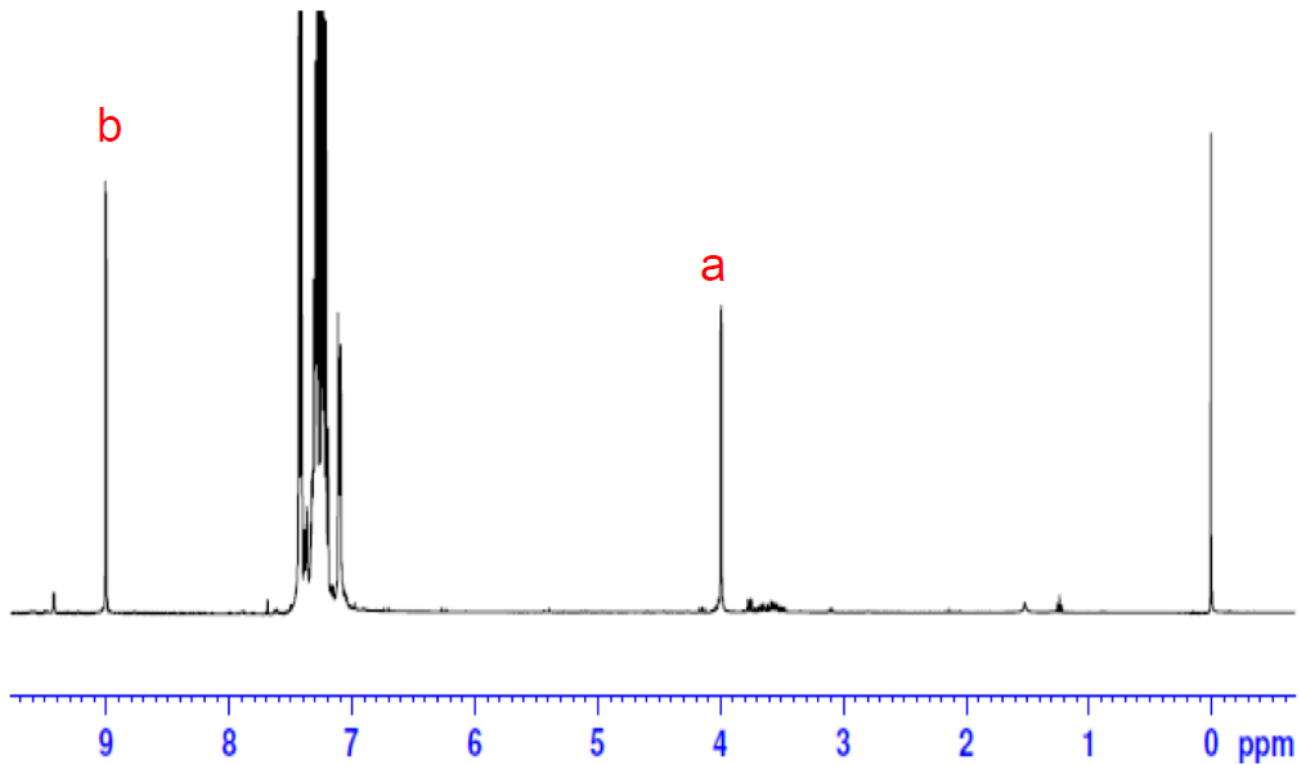
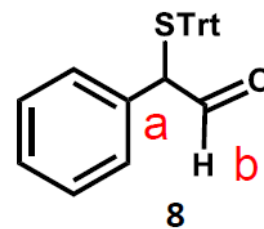
$^1\text{H}$ NMR

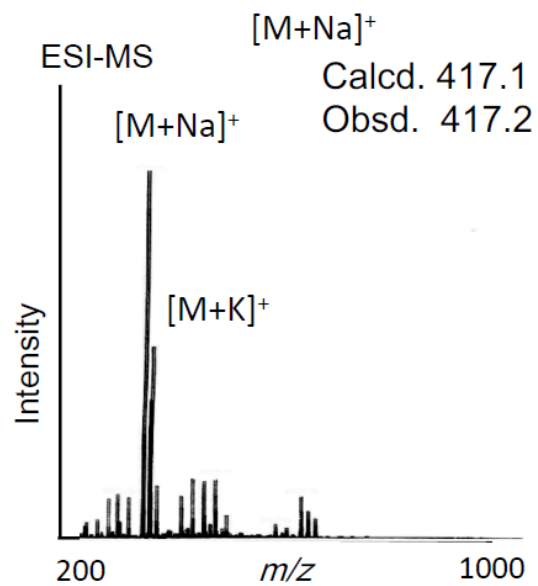
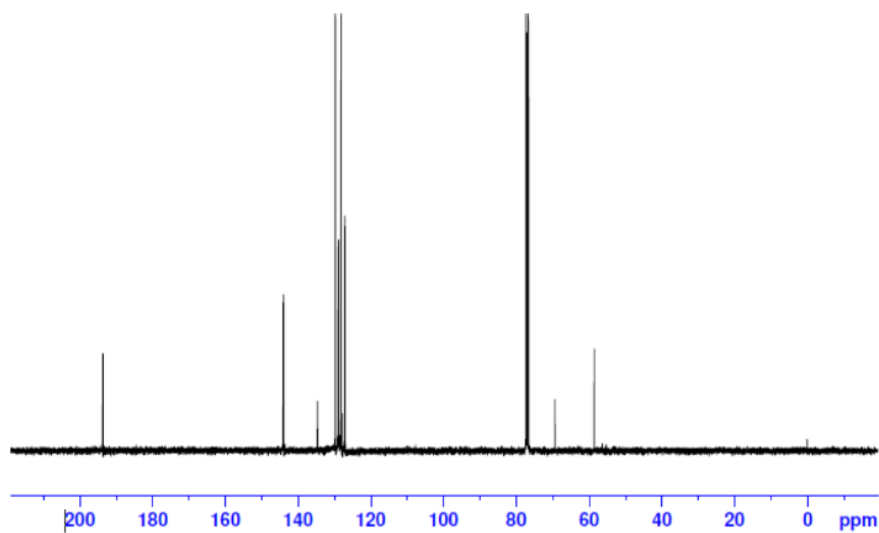
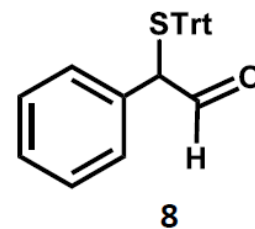
 $^{13}\text{C}$ NMR



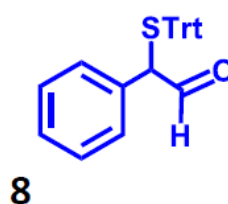
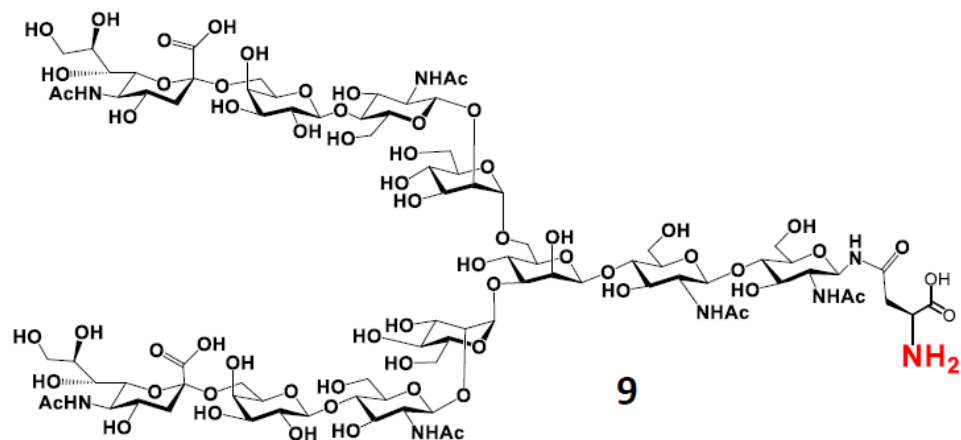
$^1\text{H}$ NMR

 $^{13}\text{C}$ NMR

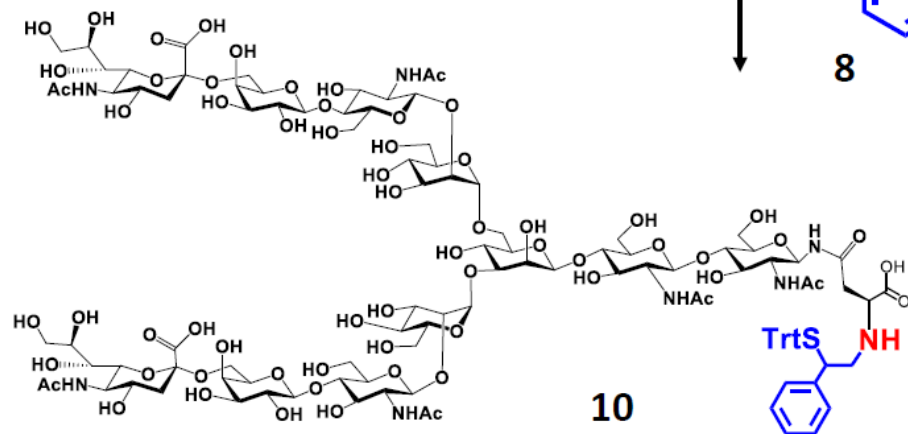
$^1\text{H}$ NMR

$^{13}\text{C}$ NMR

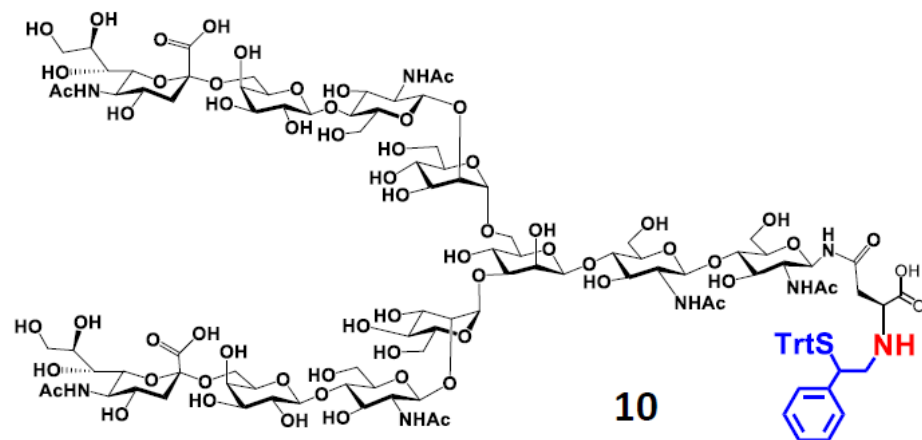
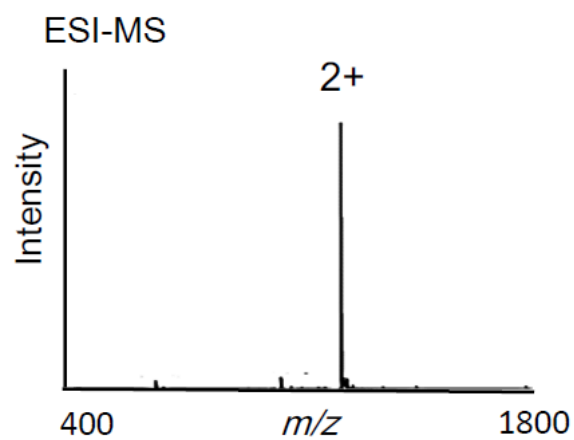
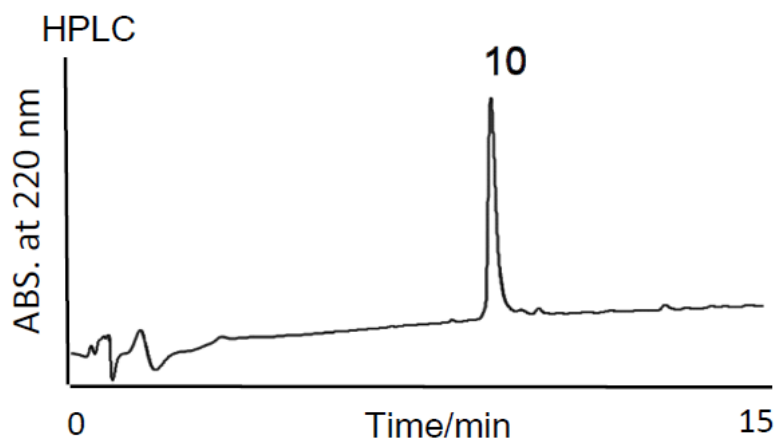
## Incorporation of Auxiliary Group to N-glycan



Pic·BH<sub>3</sub>  
DMF/H<sub>2</sub>O/*i*PrOH  
HCOOH

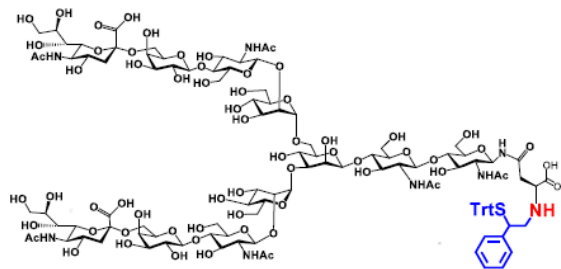
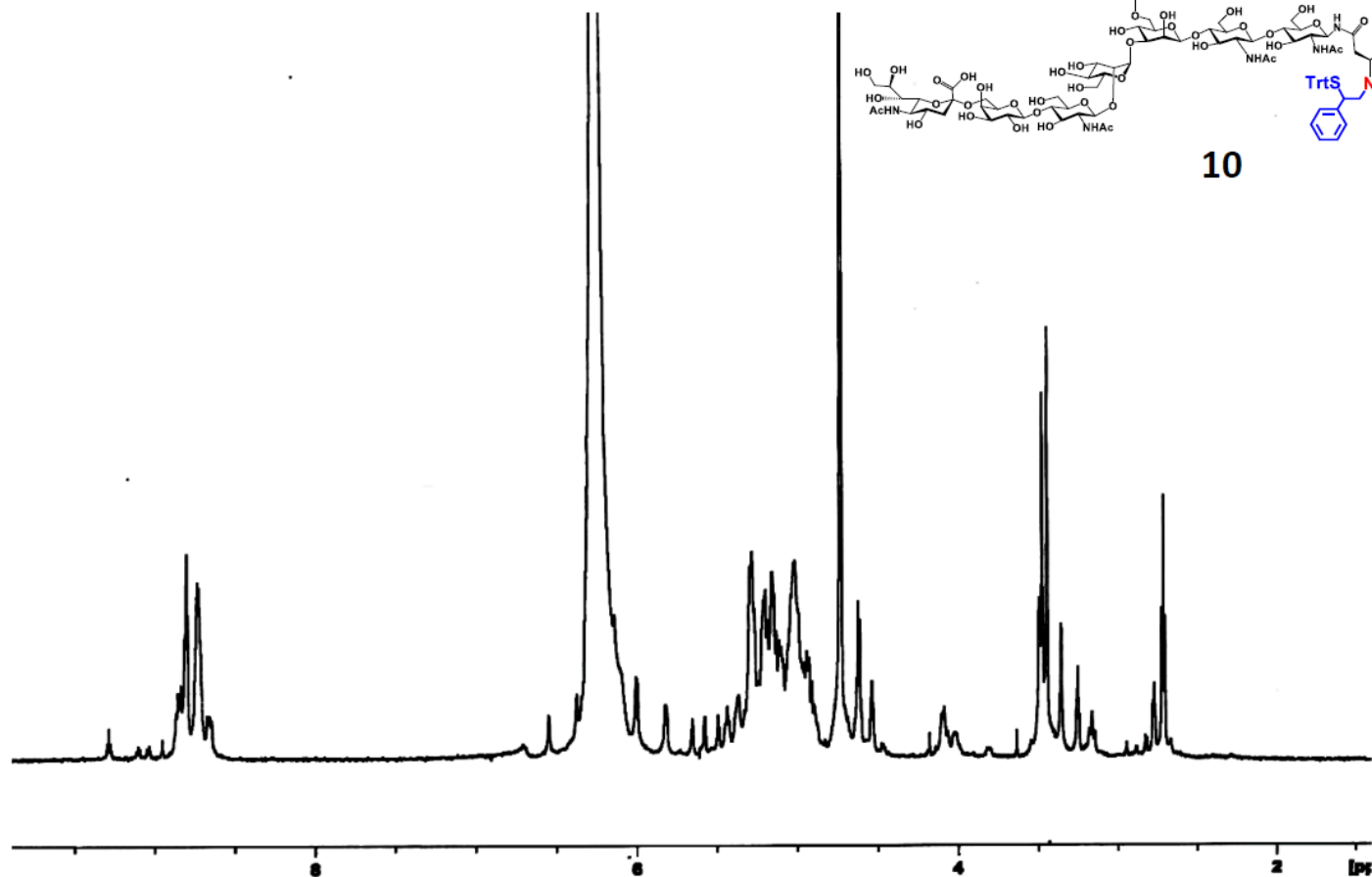


## Incorporation of Auxiliary Group to N-glycan

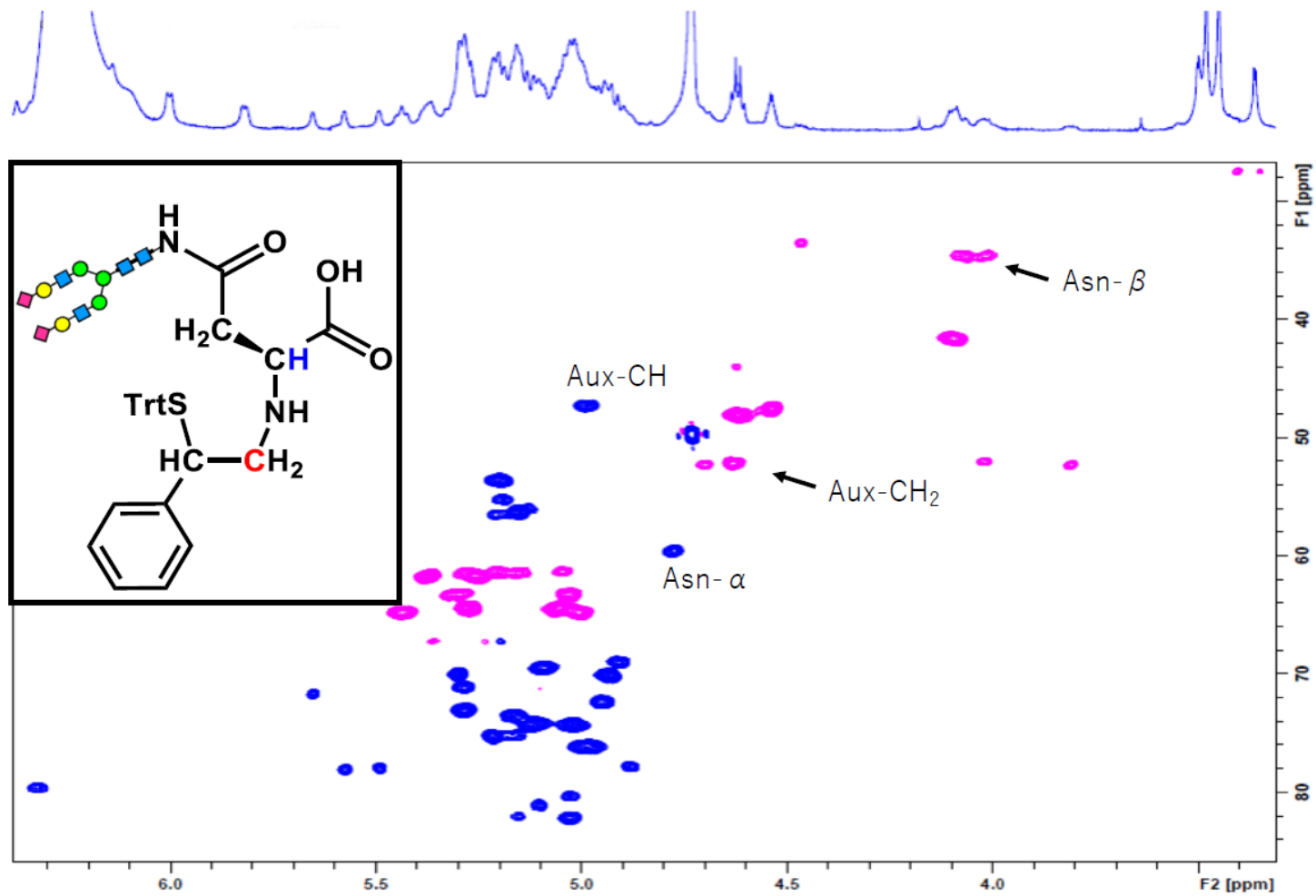


Calcd. 2716.0  
Obsd. 2715.8

yield 55%

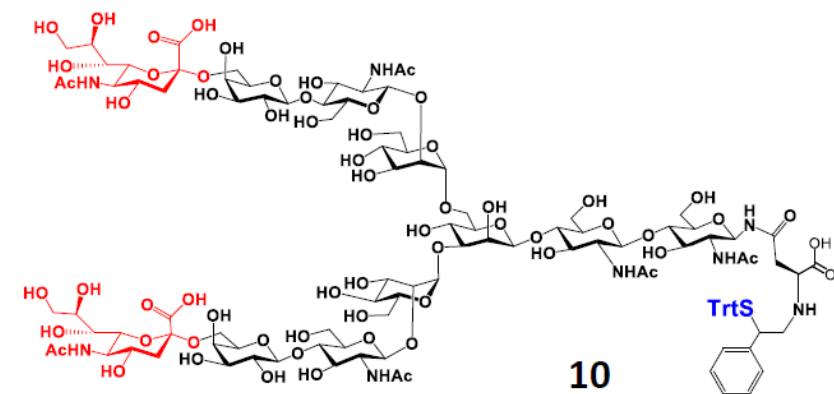
$^1\text{H}$ NMR (700MHz)**10**

## HSQC NMR (700MHz)

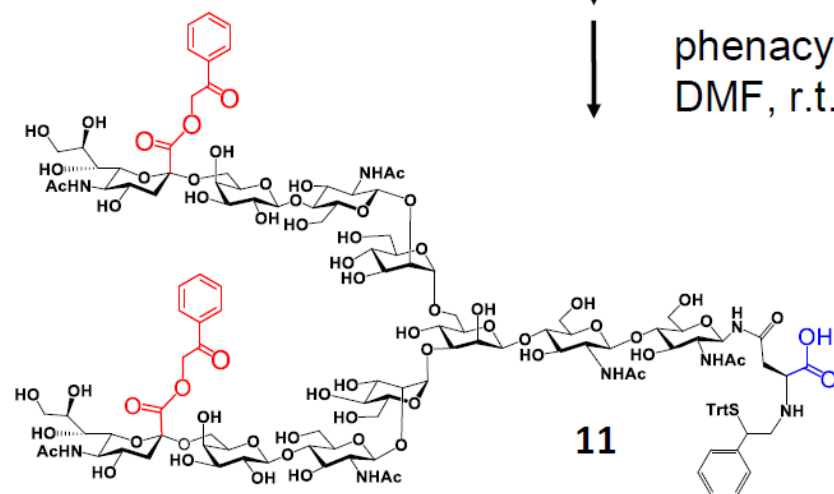




## Protection of sialic acids

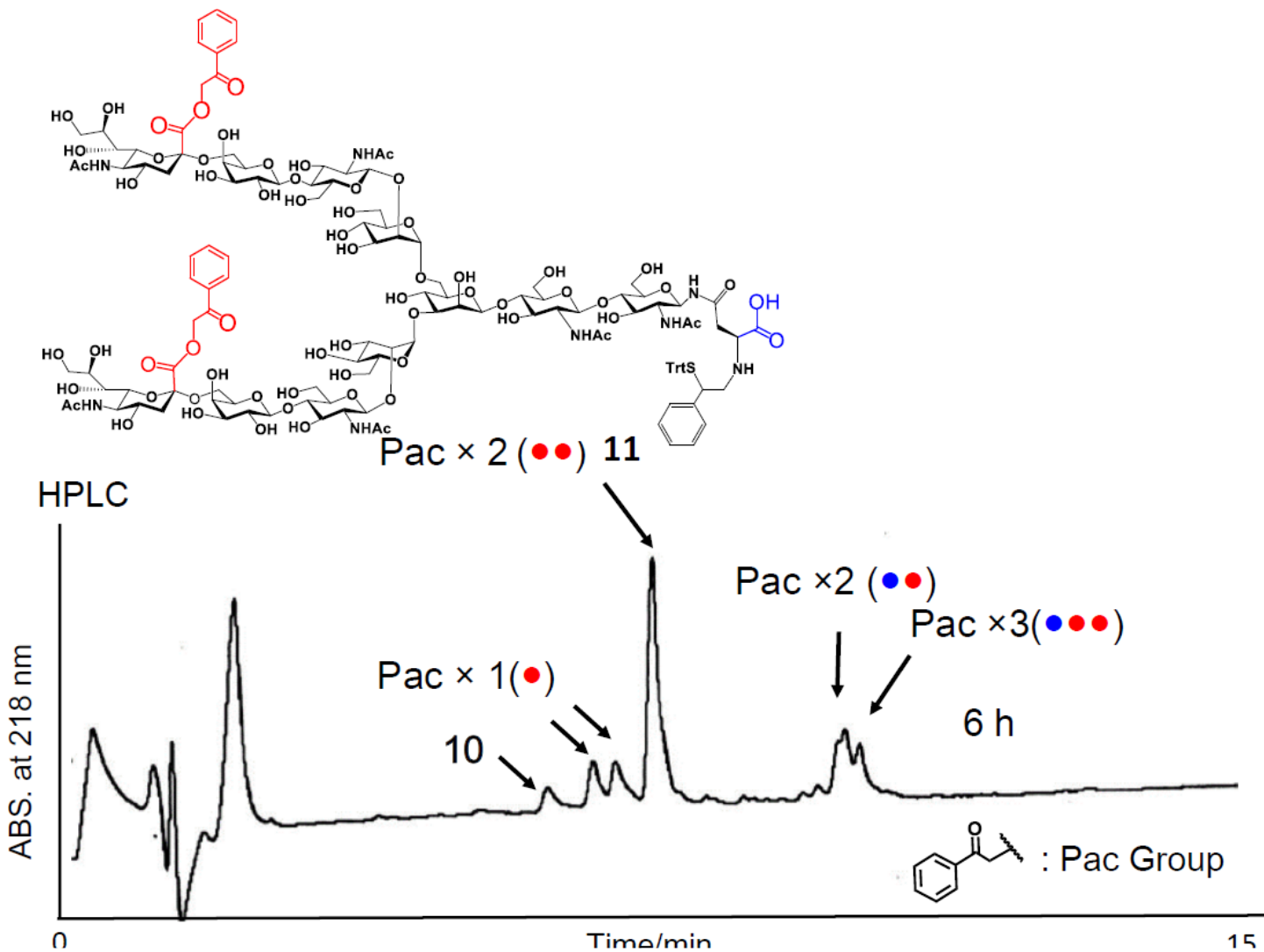


↓ adjusted to pH 4.0 by  $\text{Cs}_2\text{CO}_3$   
↓ phenacyl bromide (6 eq)  
↓ DMF, r.t., 6 h

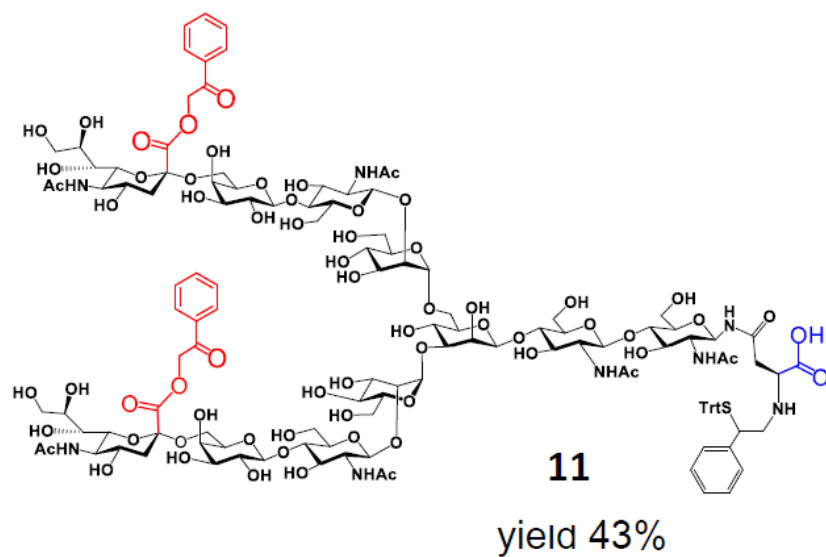
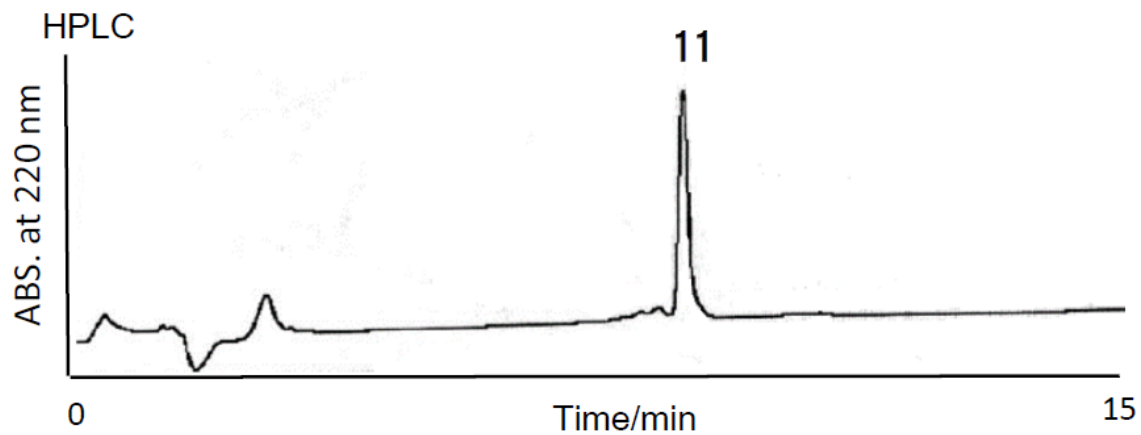


M. Murakami, *et.al.*, *Angew.Chem. Int.Ed.* **2012**, *51*, 3567-3572

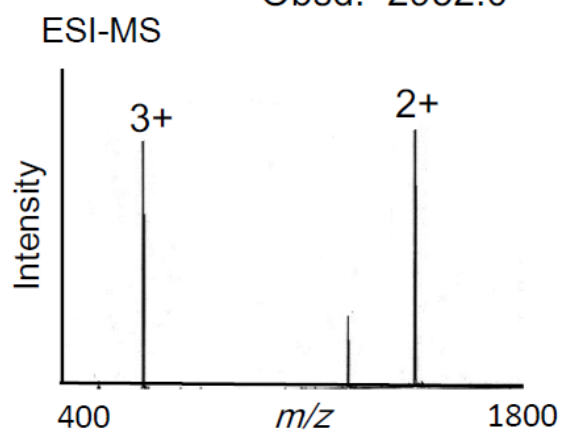
## Protection of sialic acids



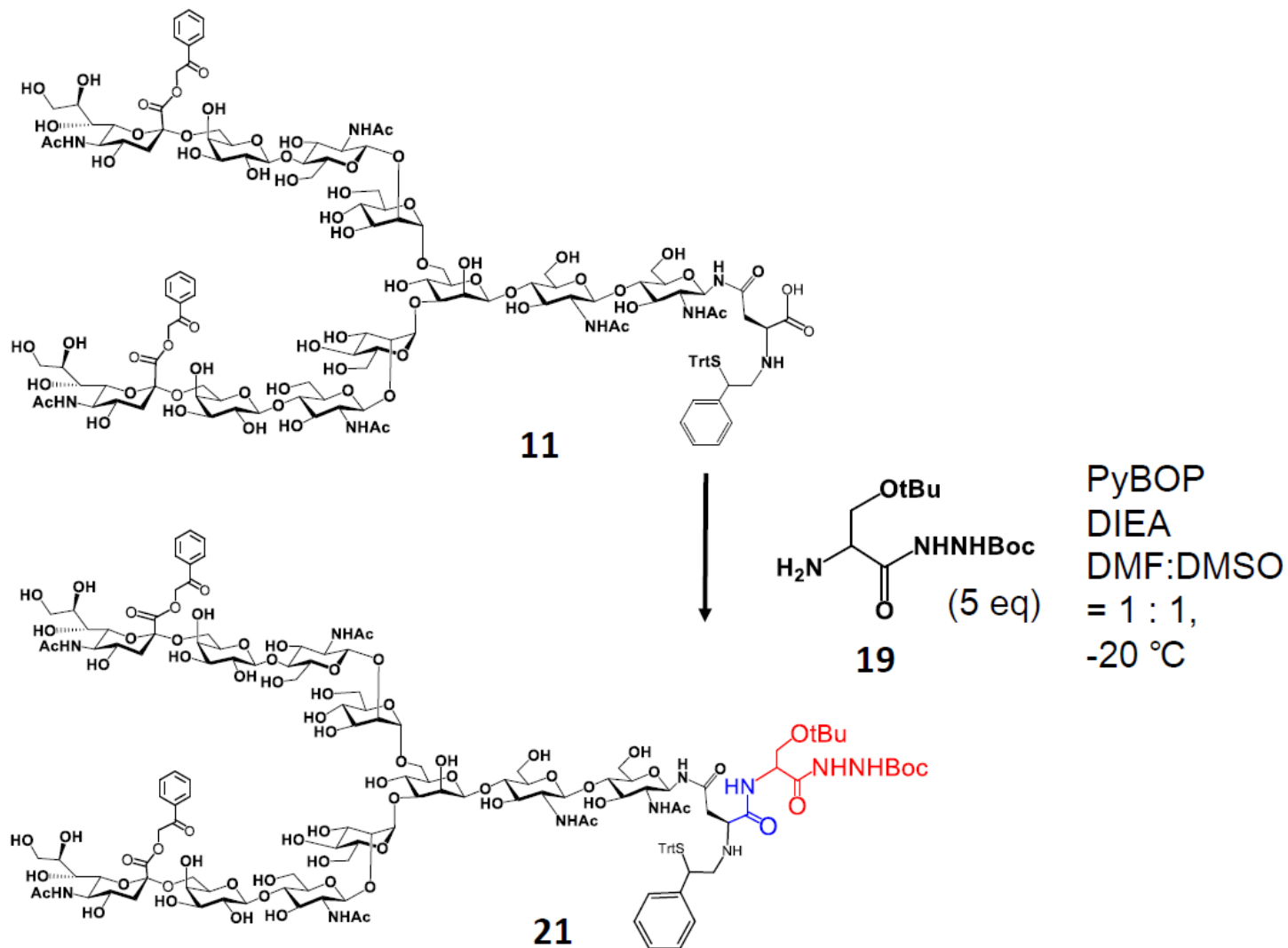
## Protection of sialic acids



Calcd. 2951.1  
Obsd. 2952.0

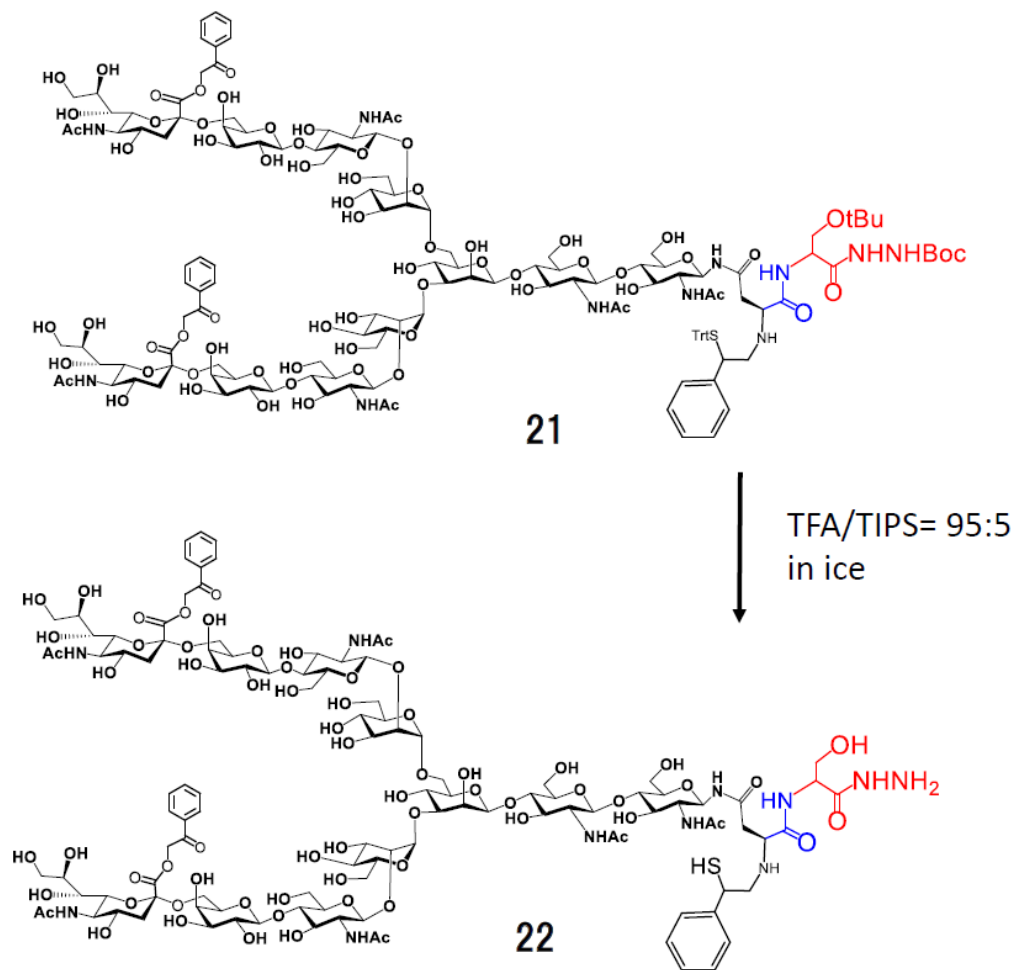


## Coupling Reaction





## Deprotection



Calcd. 2811.0  
Obsd. 2810.9

