

# Multi-Component One-pot Synthesis of the Tumor-Associated Carbohydrate Antigen Globo-H Based on Pre-activation of Thioglycosyl Donors

## Supporting Information

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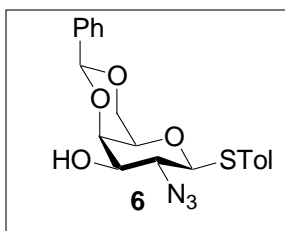
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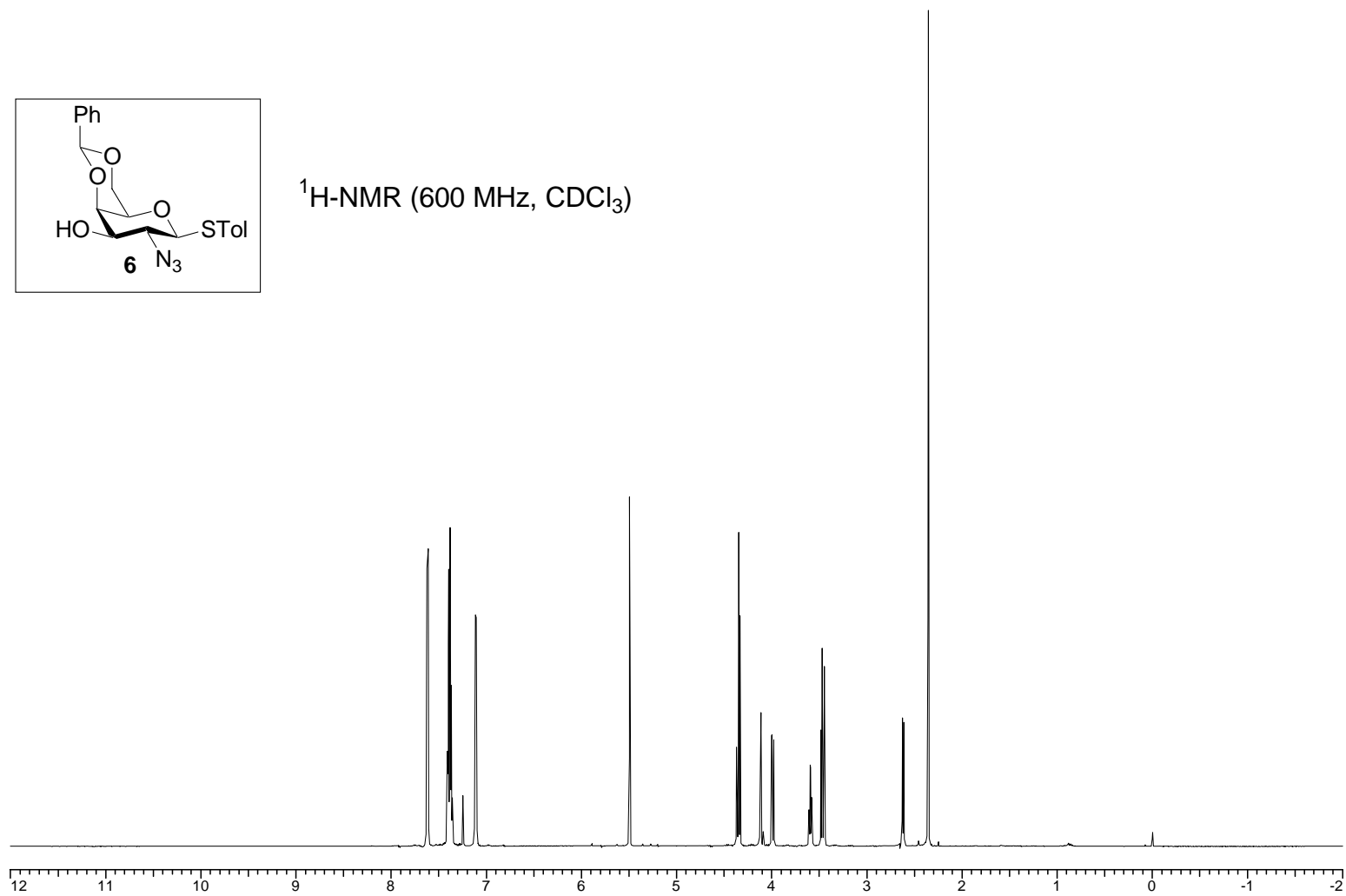


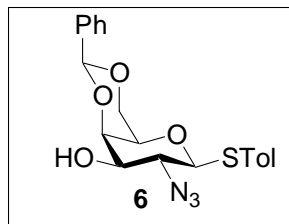
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**General Experimental Procedures.** All reactions were carried out under nitrogen with anhydrous solvents in flame-dried glassware, unless otherwise noted. All glycosylation reactions were performed in the presence of molecular sieves, which were flame-dried right before the reaction under high vacuum. Glycosylation solvents were dried using an solvent purification system and used directly without further drying. Chemicals used were reagent grade as supplied except where noted. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates; Compound spots were visualized by UV light (254 nm) and by staining with a yellow solution containing  $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$  (0.5 g) and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  (24.0 g) in 6%  $\text{H}_2\text{SO}_4$  (500 mL). Flash column chromatography was performed on silica gel 60 (230–400 Mesh). NMR spectra were referenced using  $\text{Me}_4\text{Si}$  (0 ppm), residual  $\text{CHCl}_3$  ( $\delta$   $^1\text{H}$ -NMR 7.26 ppm,  $^{13}\text{C}$ -NMR 77.0 ppm). Peak and coupling constant assignments are based on  $^1\text{H}$ -NMR,  $^1\text{H}$ - $^1\text{H}$  gCOSY and (or)  $^1\text{H}$ - $^{13}\text{C}$  gHMQC and  $^1\text{H}$ - $^{13}\text{C}$  gHMBC experiments. All optical rotations were measured at 25 °C using the sodium D line. ESI mass spectra were recorded in positive ion mode. High-resolution mass spectra were recorded on a Micromass electrospray mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode.

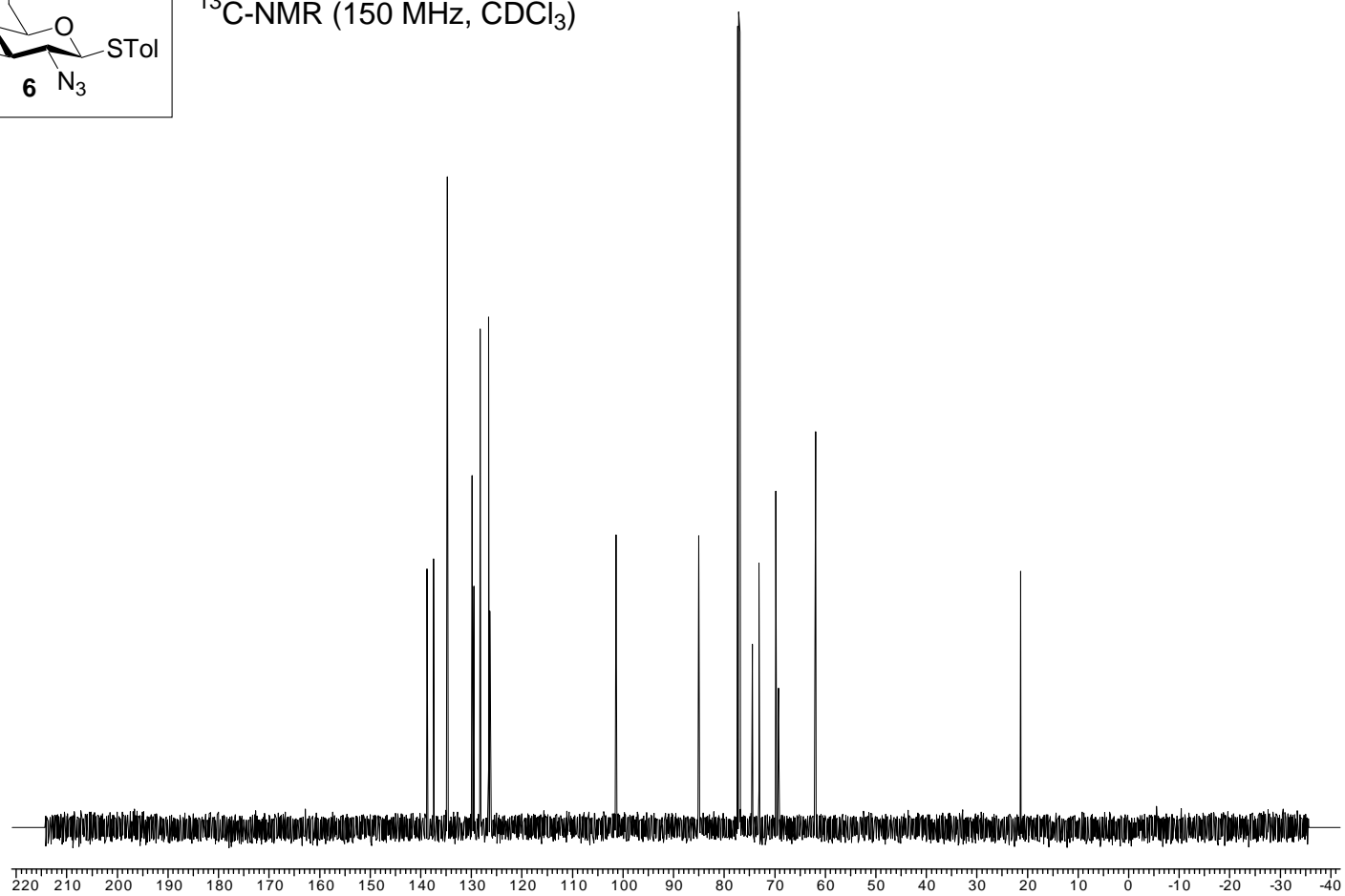


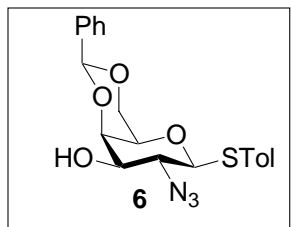
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)



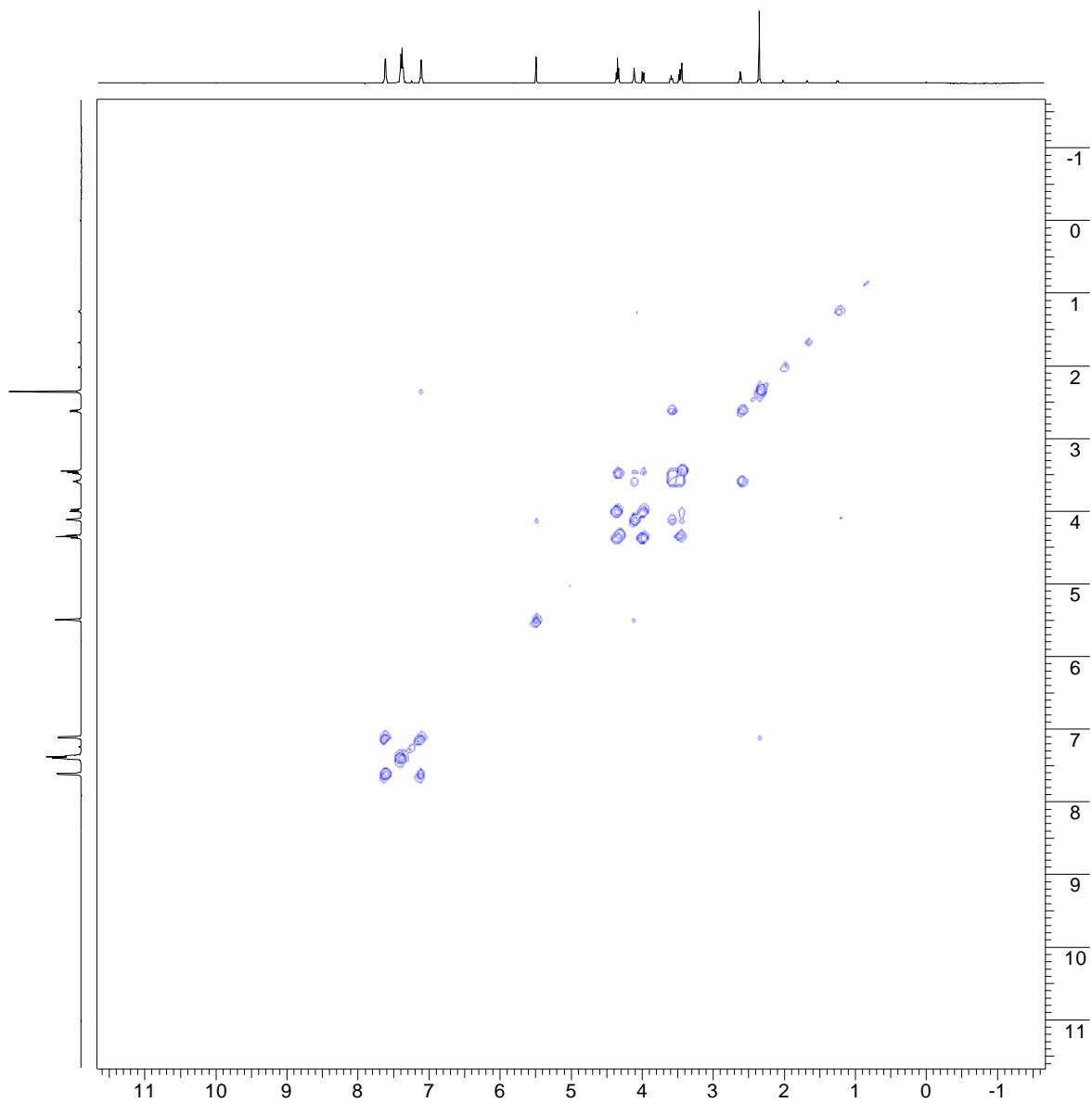


<sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>)

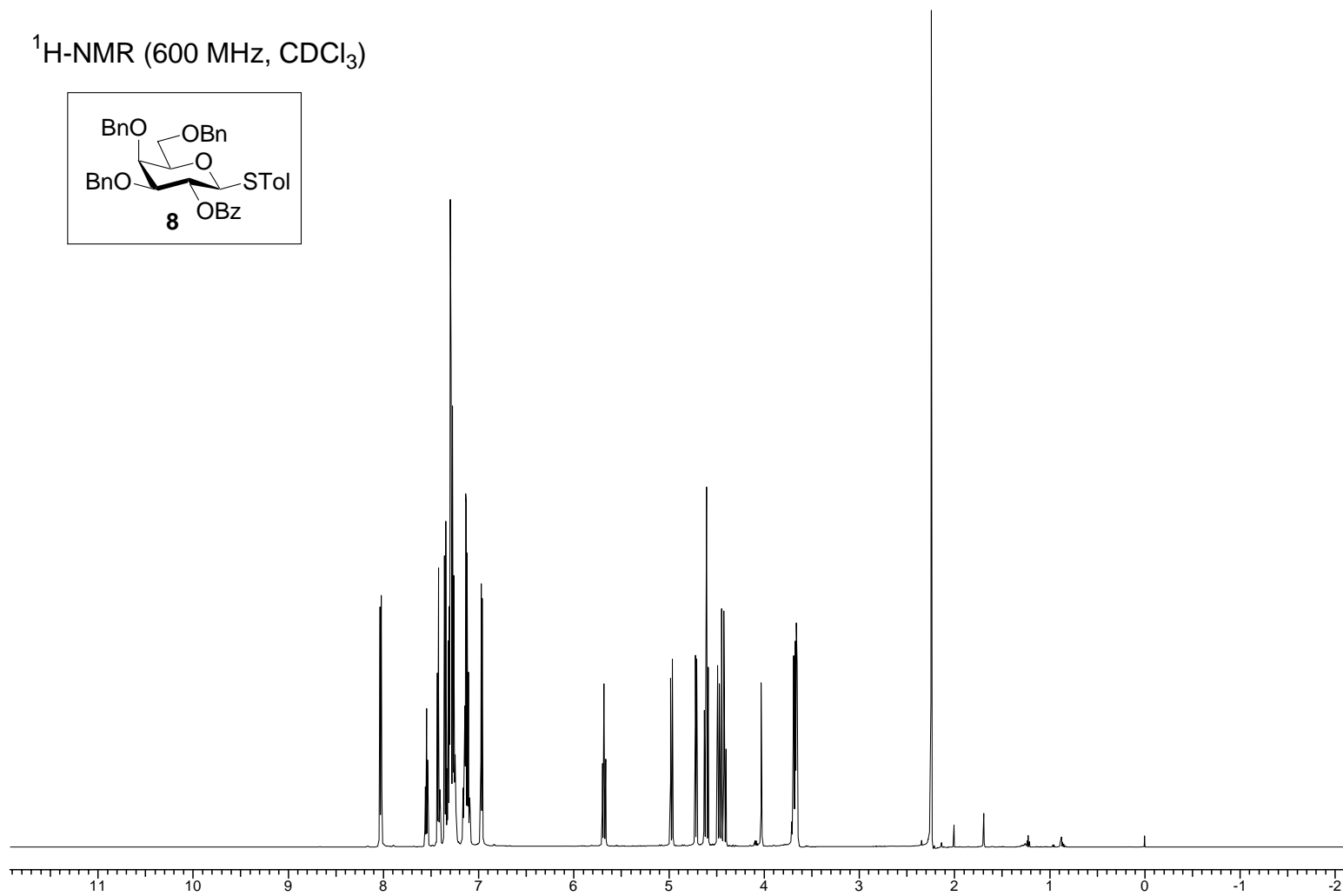
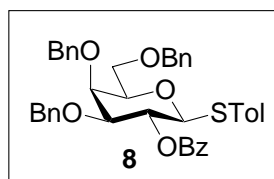




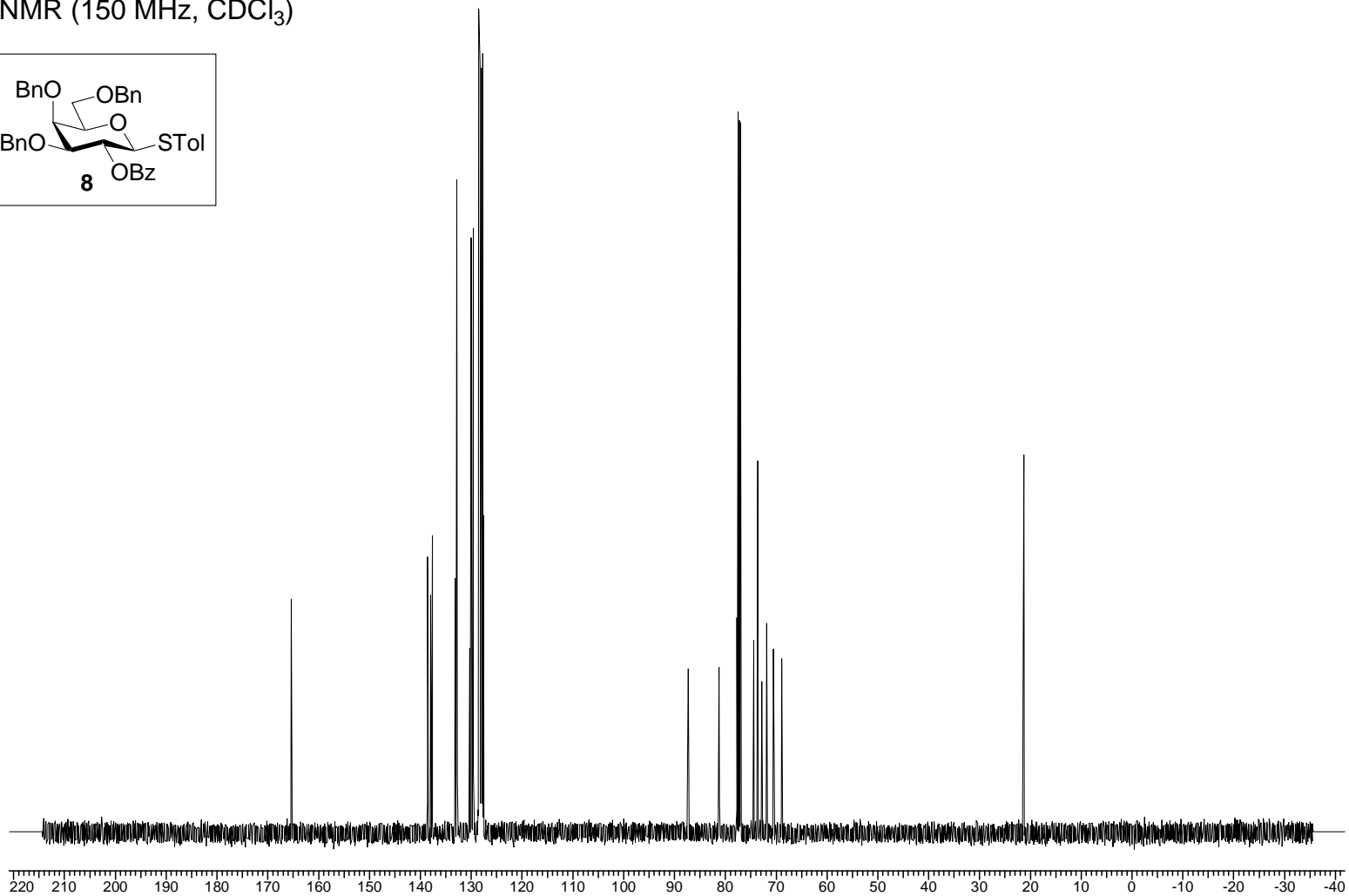
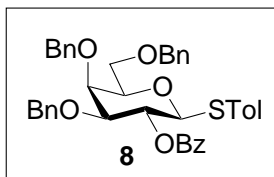
gCOSY(600 MHz, CDCl<sub>3</sub>)



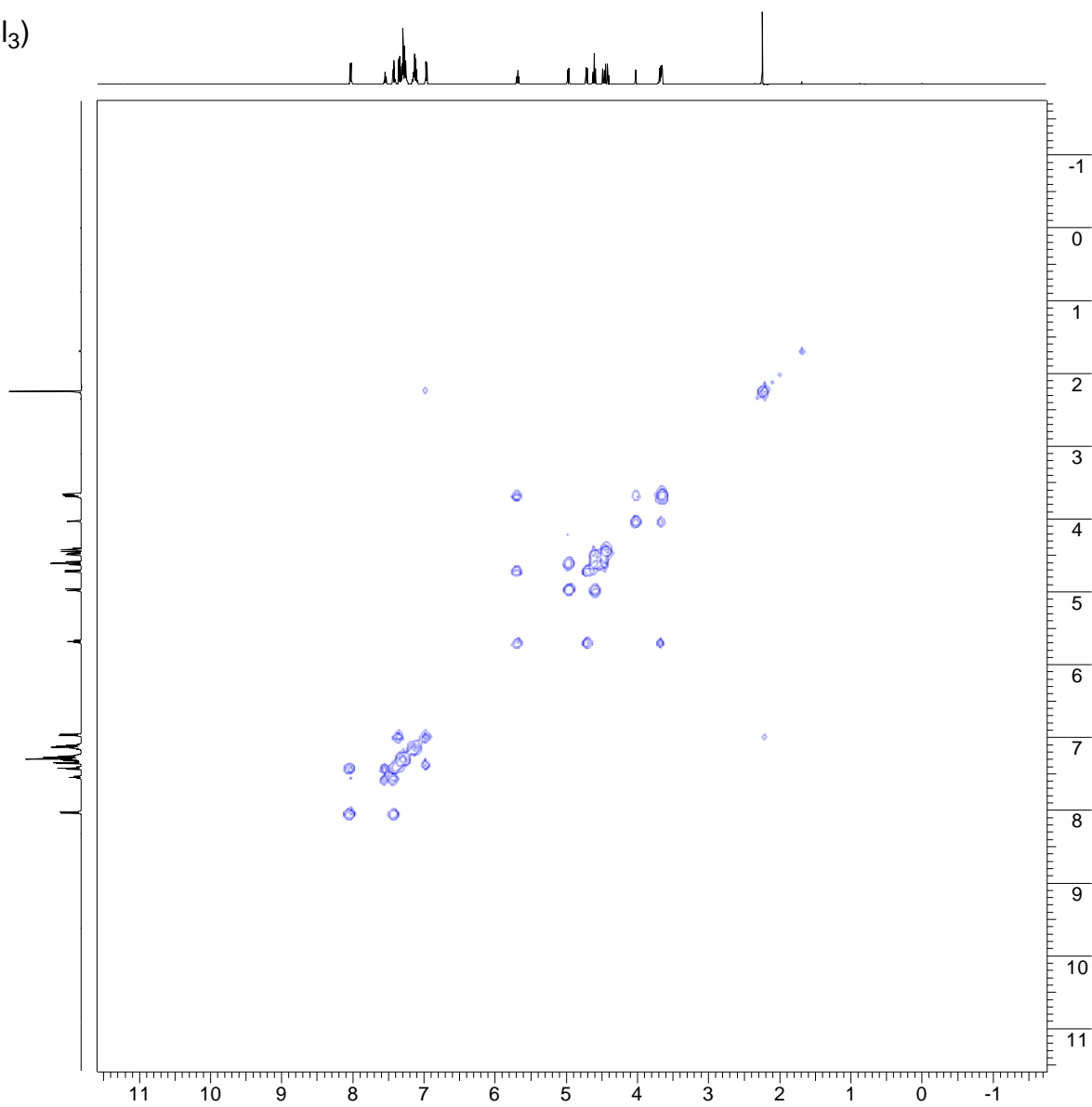
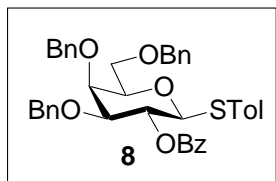
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )

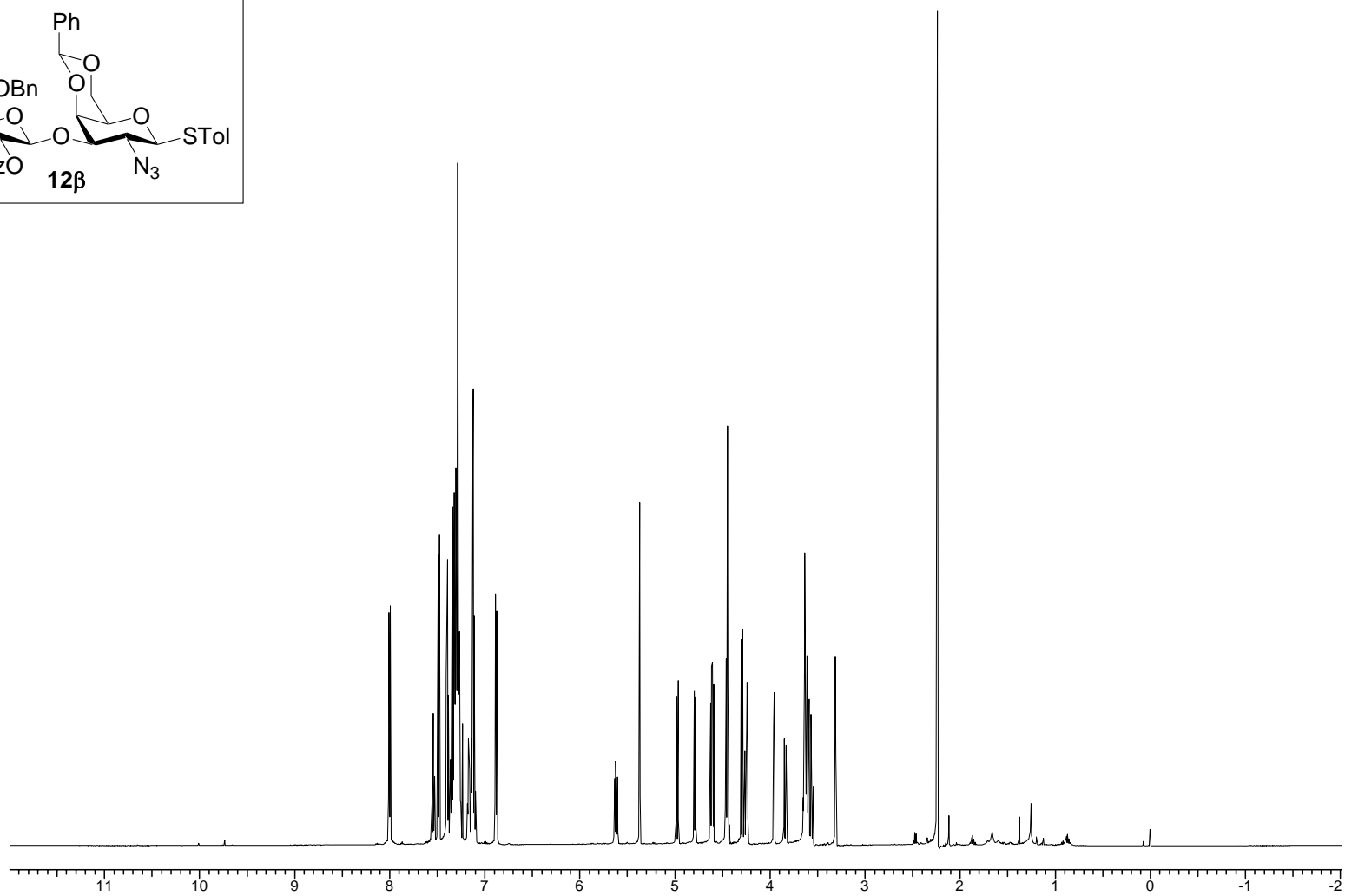
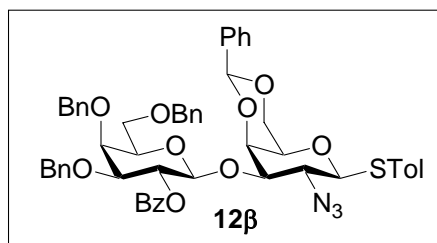


gCOSY (600 MHz, CDCl<sub>3</sub>)

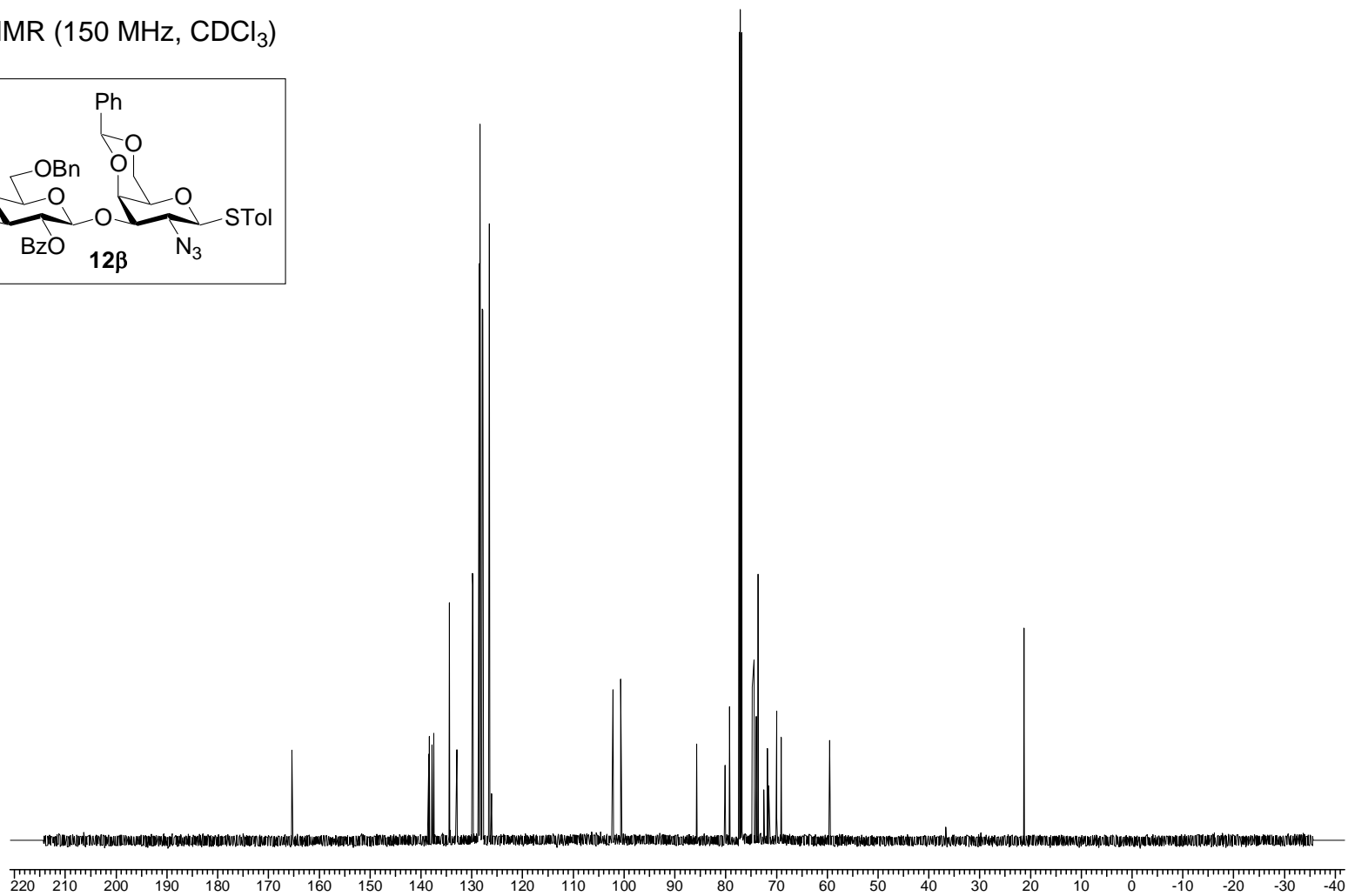
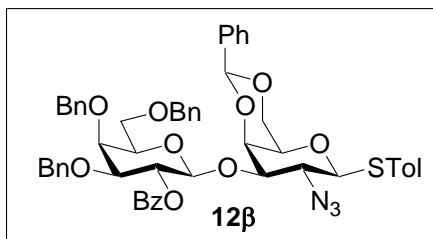




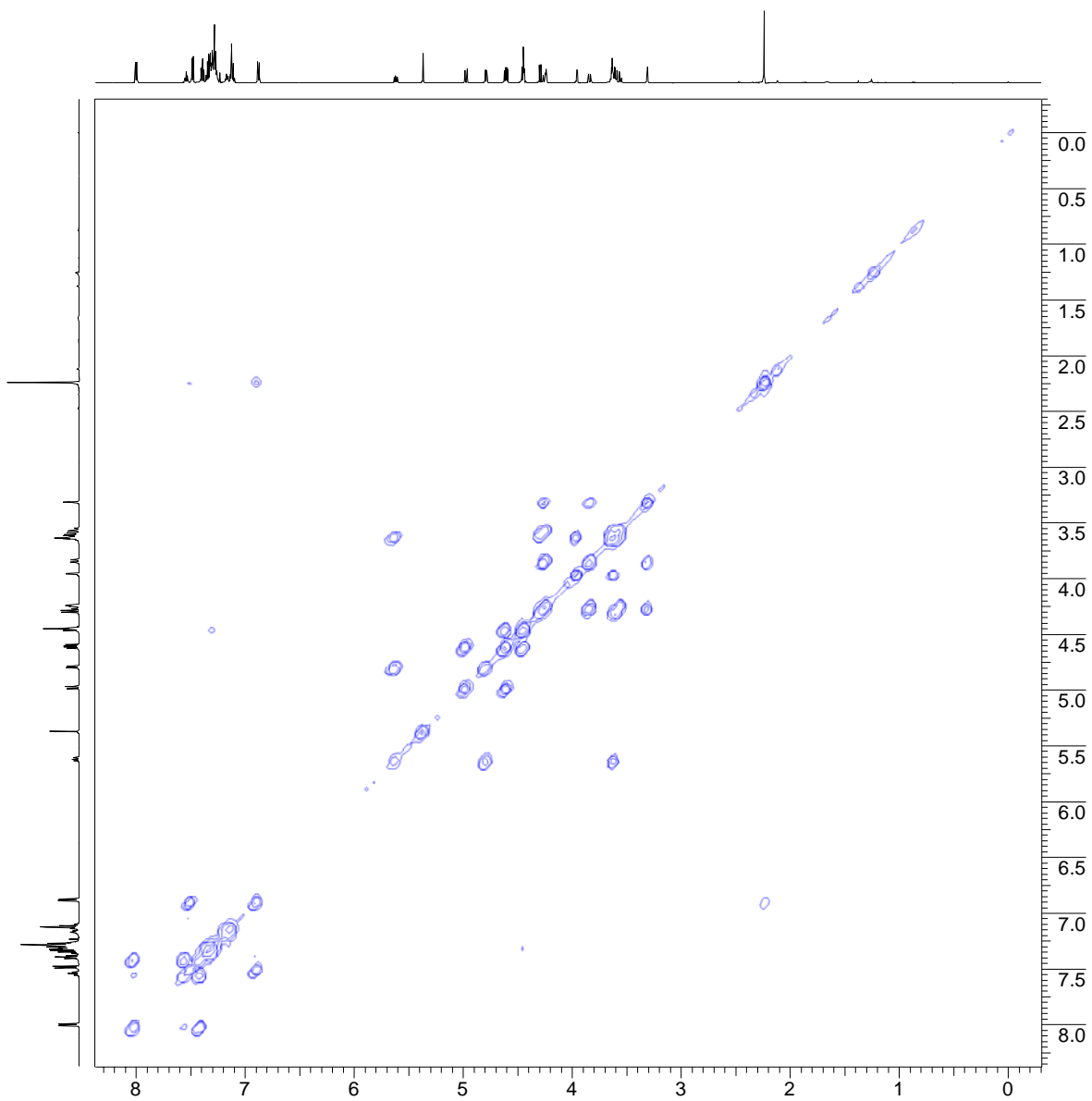
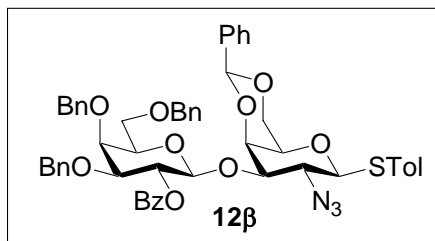
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



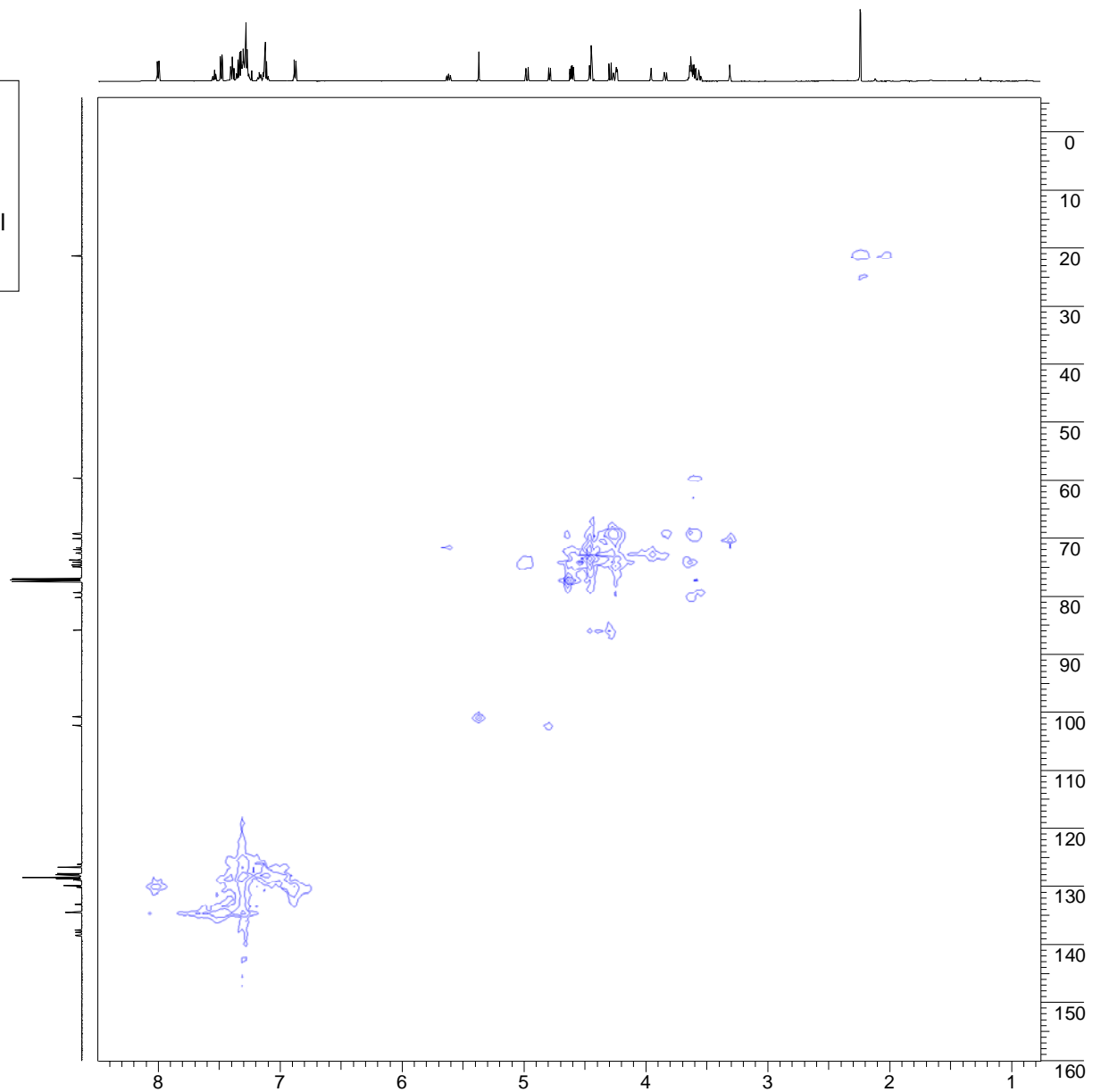
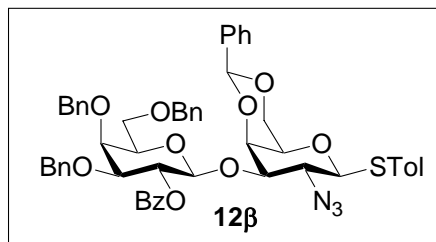
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



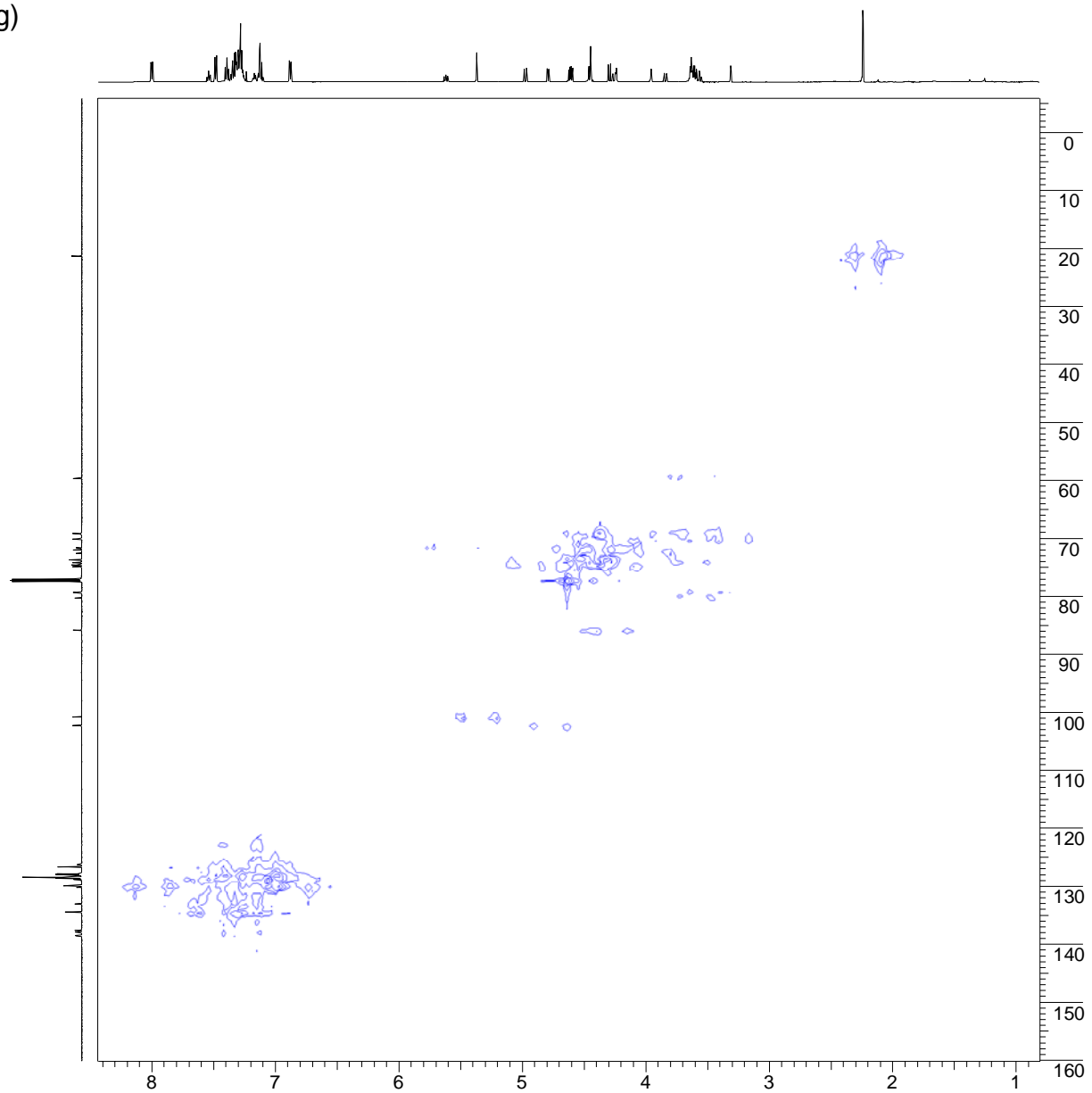
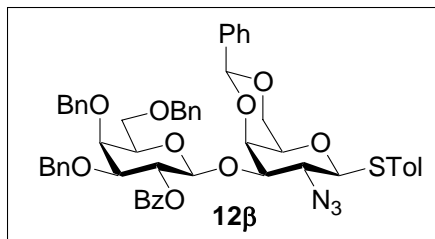
gCOSY (600 MHz, CDCl<sub>3</sub>)



gHMQC (600 MHz, CDCl<sub>3</sub>)

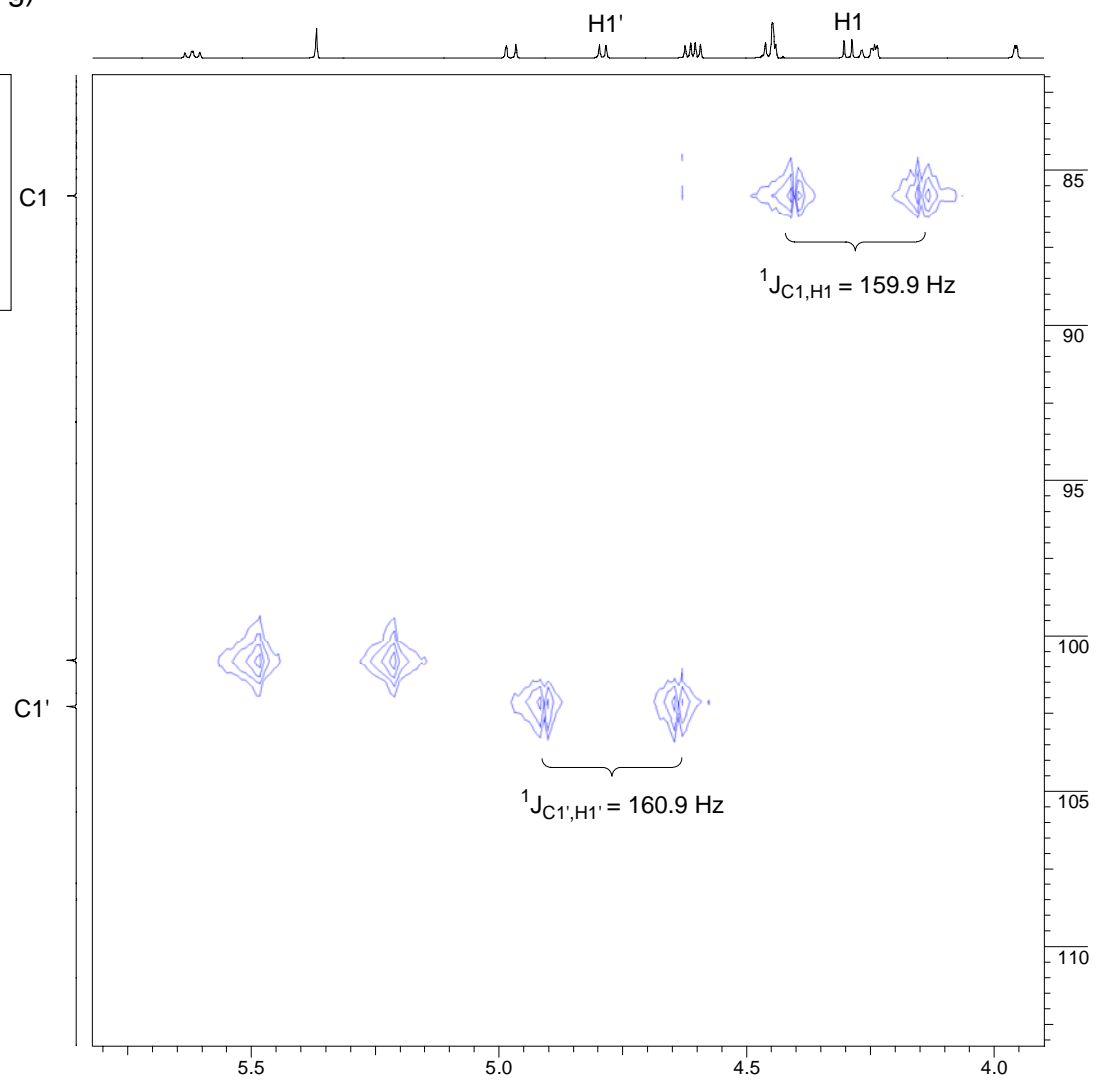
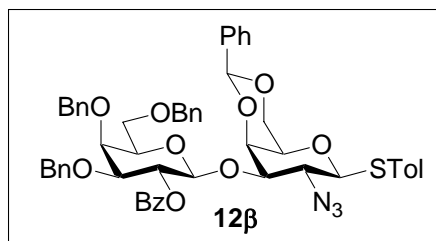


gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )

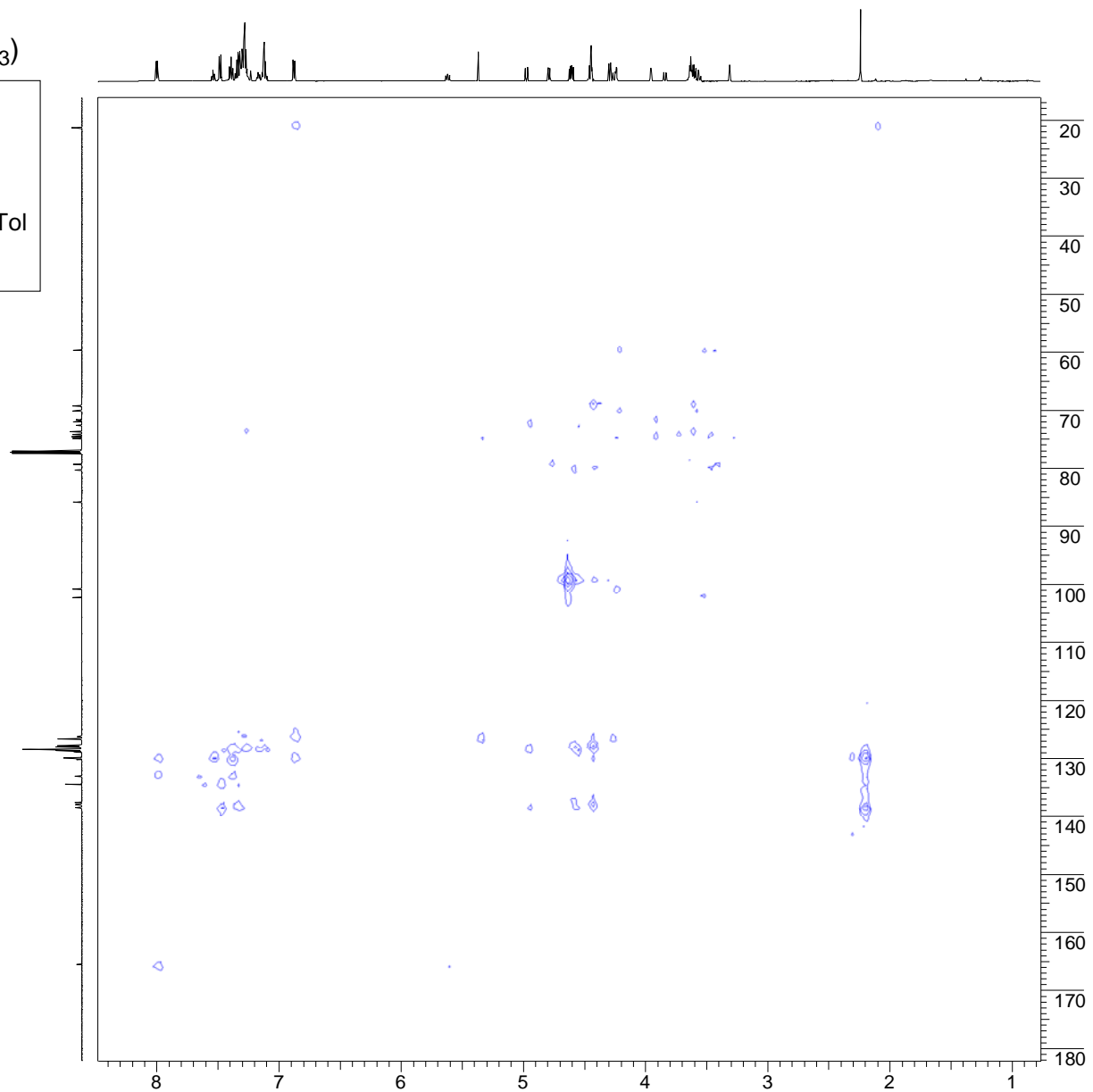
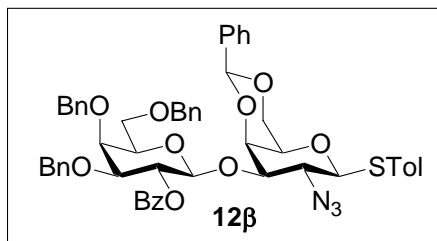


gHMQC (without  $^1\text{H}$  decoupling)

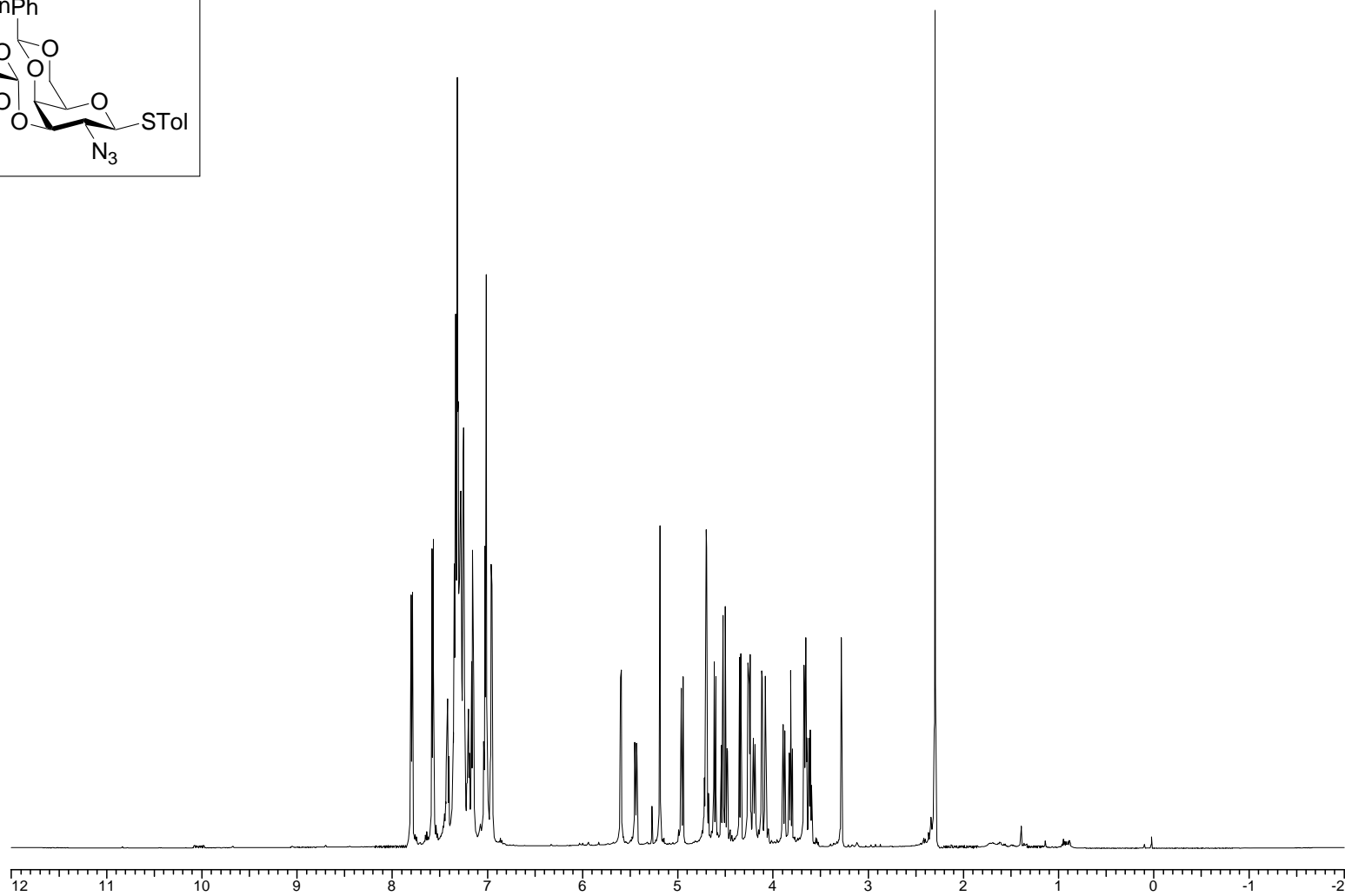
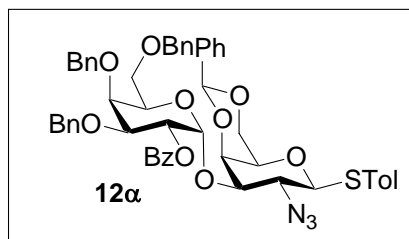
(600 MHz,  $\text{CDCl}_3$ )



gHMBC (600 MHz, CDCl<sub>3</sub>)

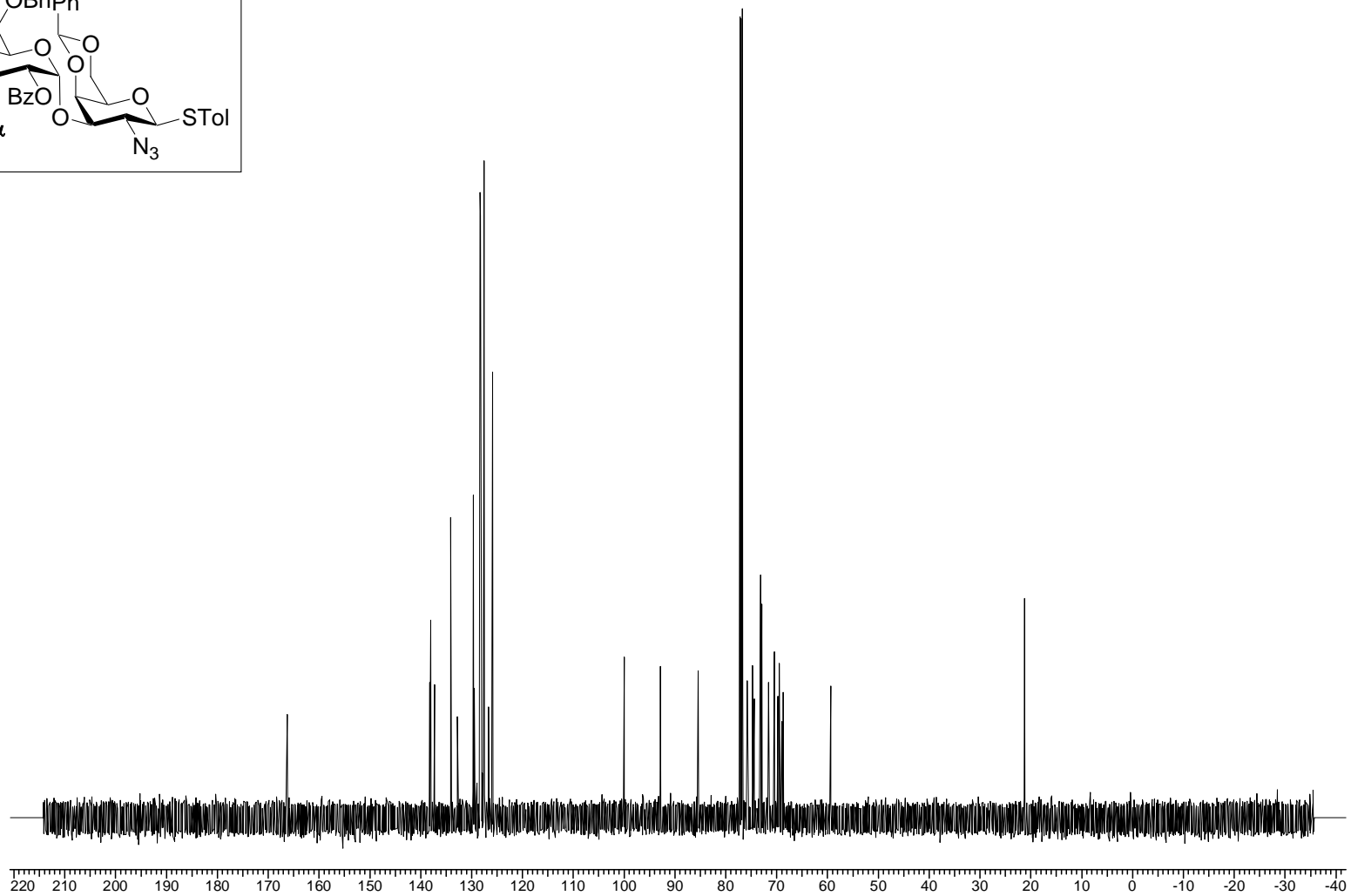
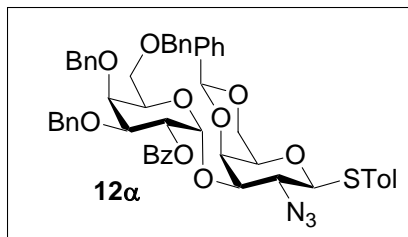


$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

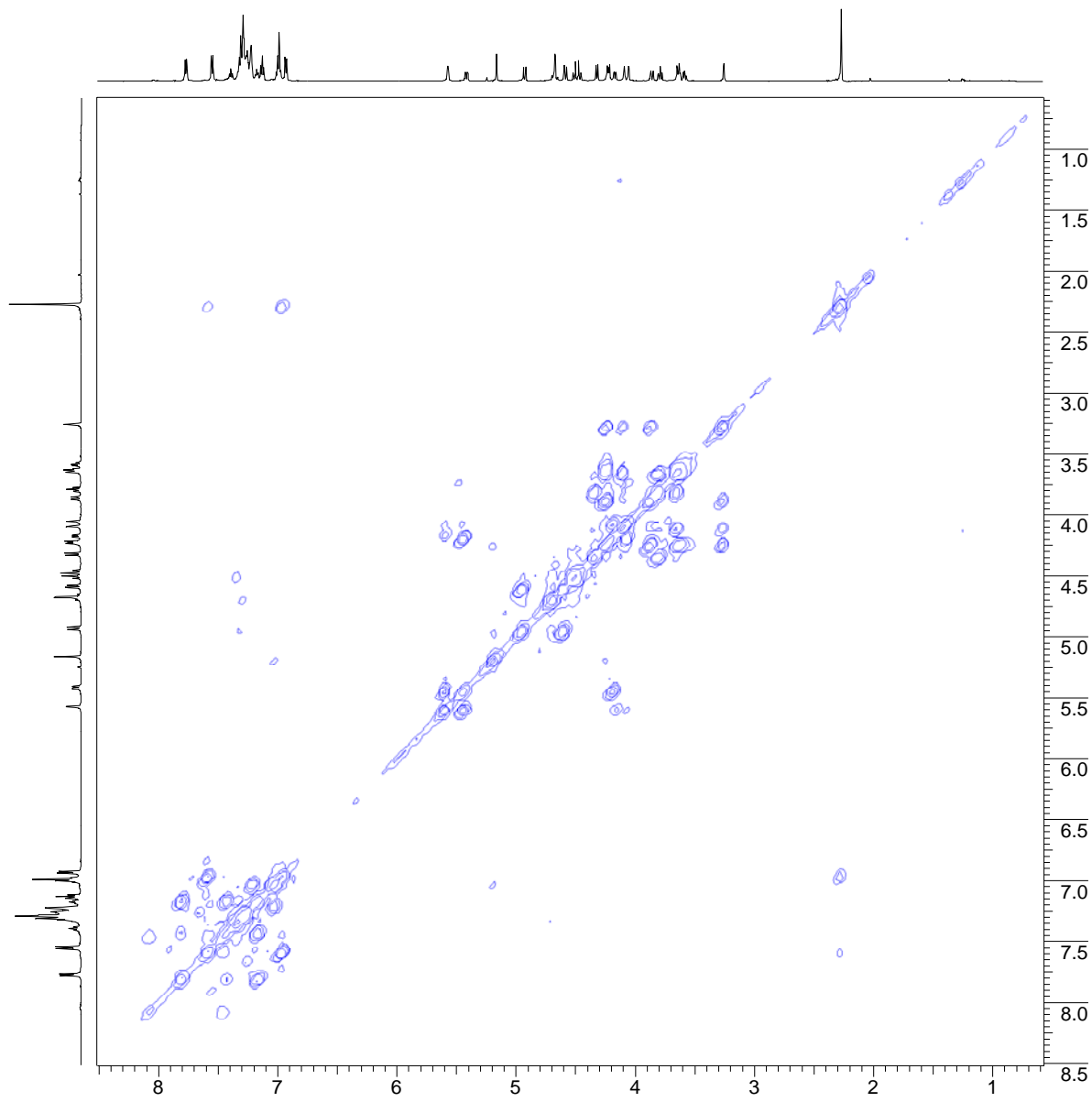
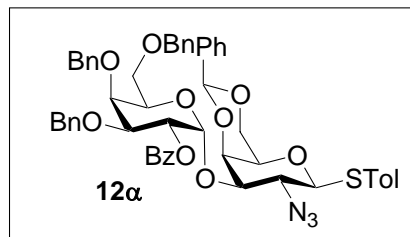




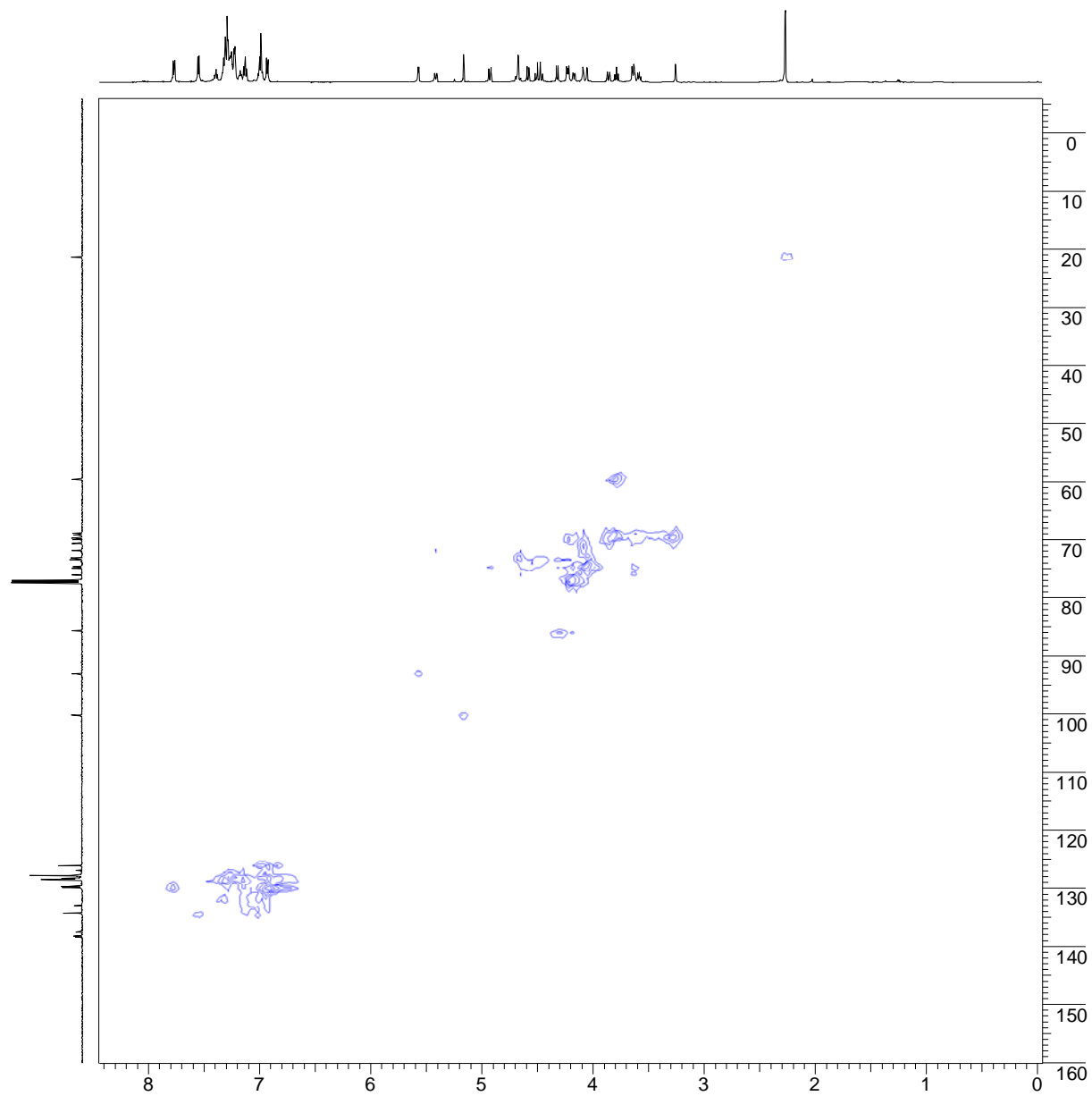
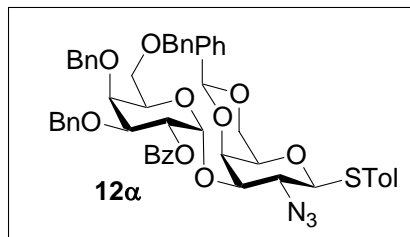
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



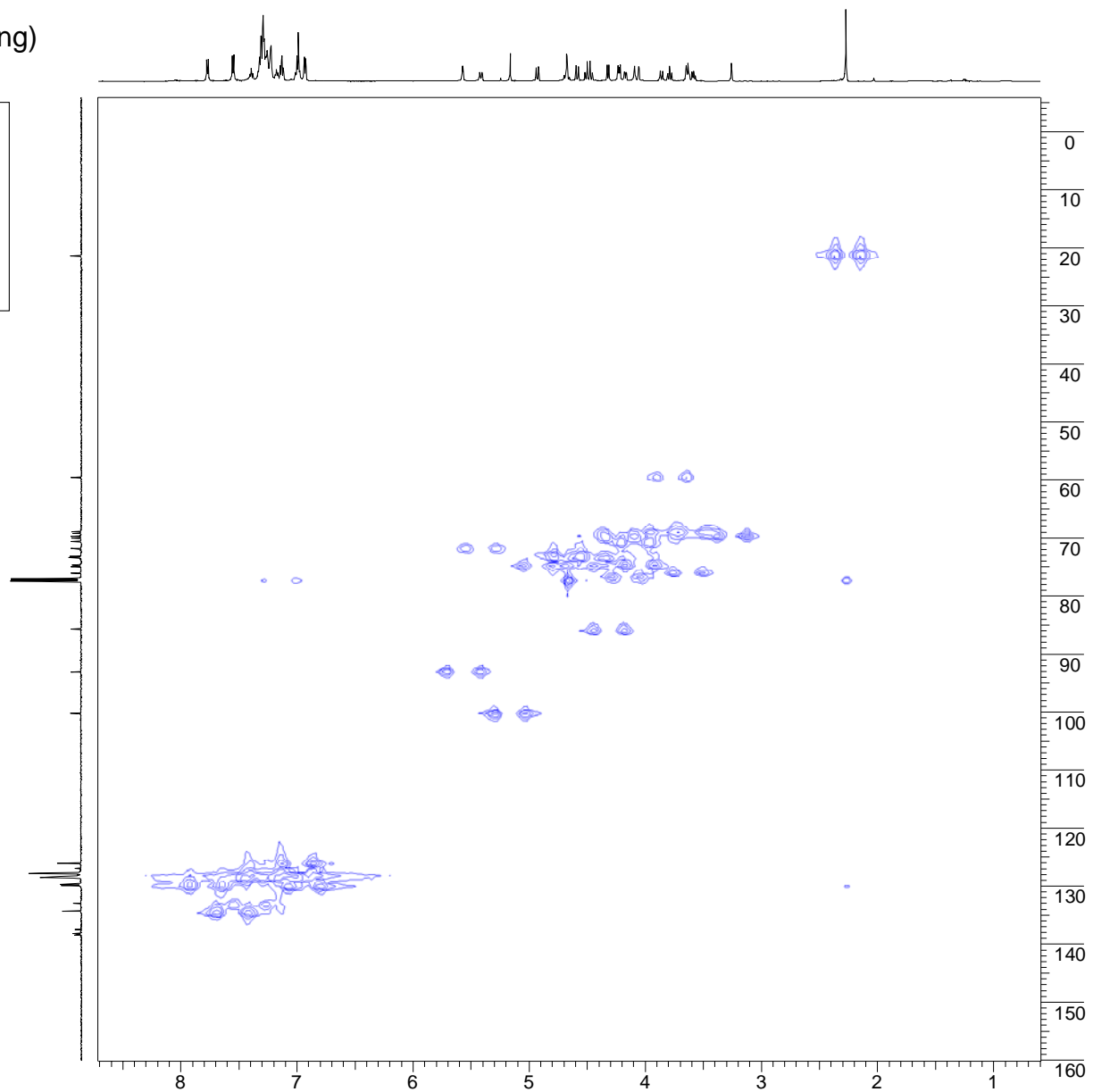
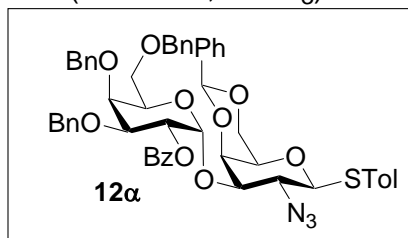
gCOSY (600 MHz, CDCl<sub>3</sub>)



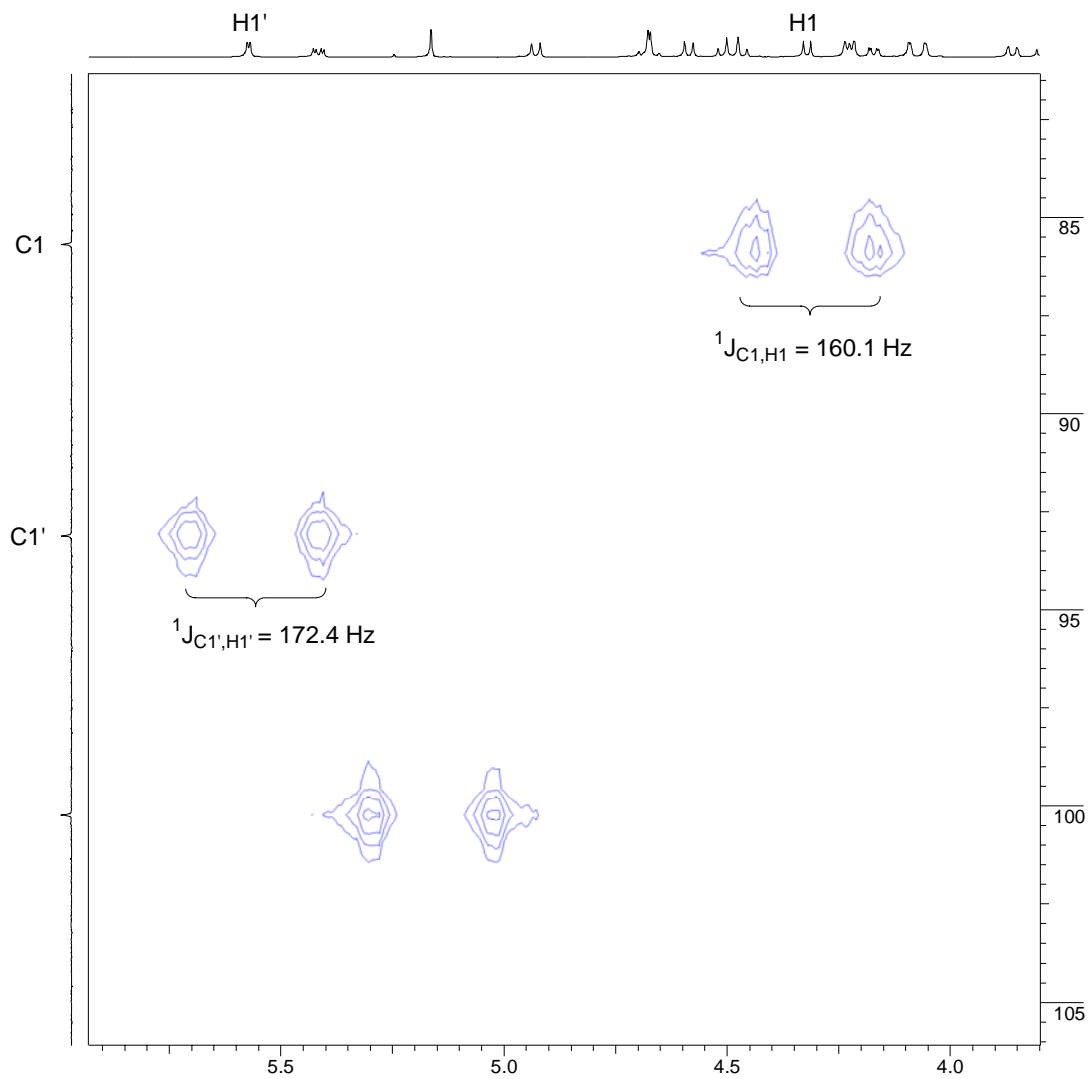
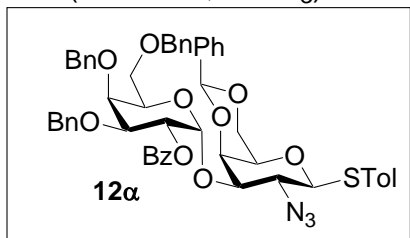
gHMQC (600 MHz, CDCl<sub>3</sub>)



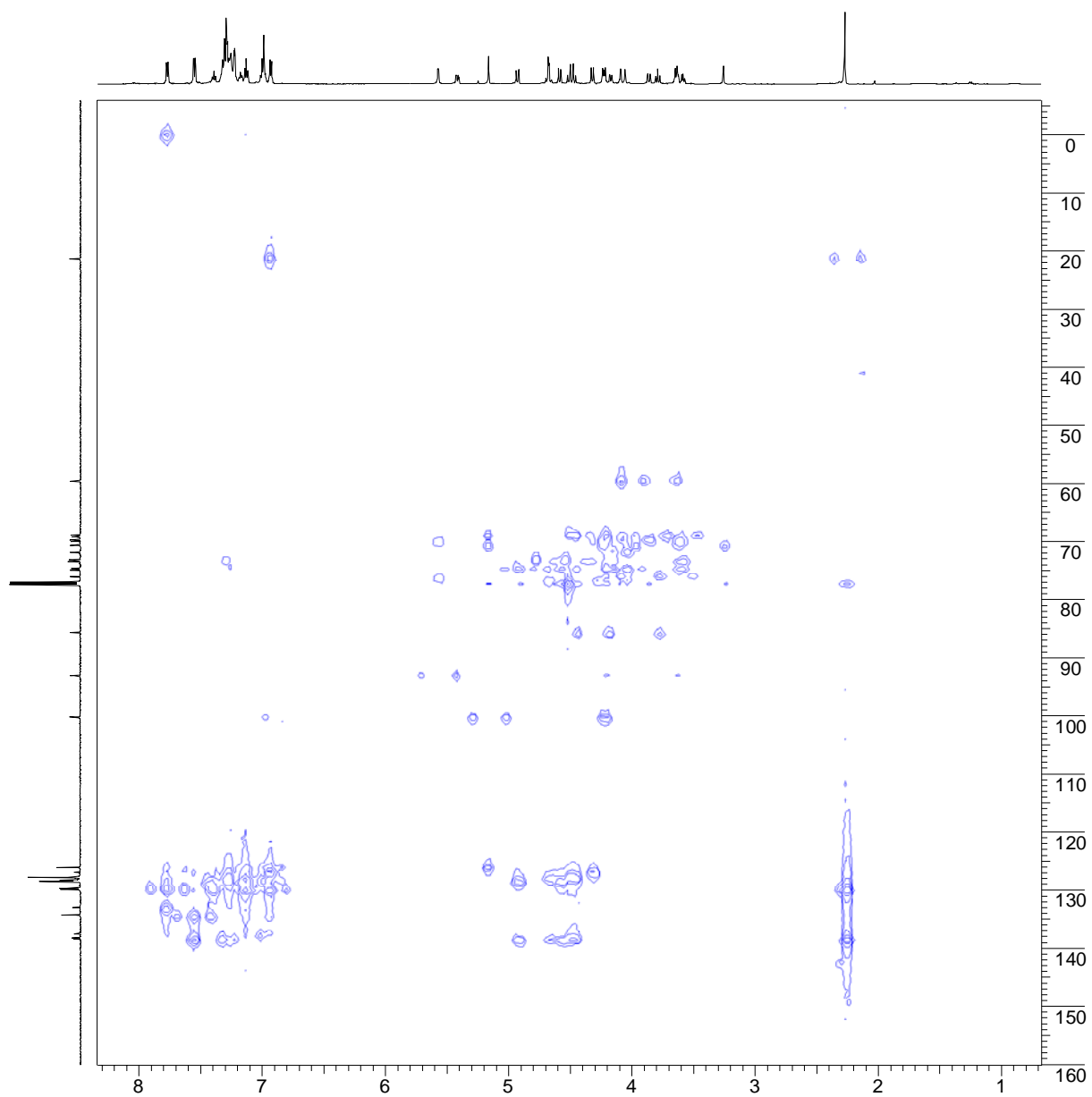
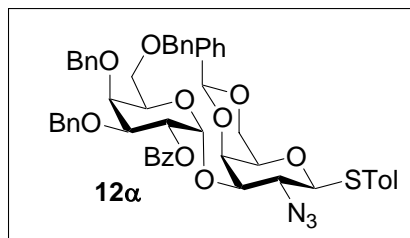
gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )



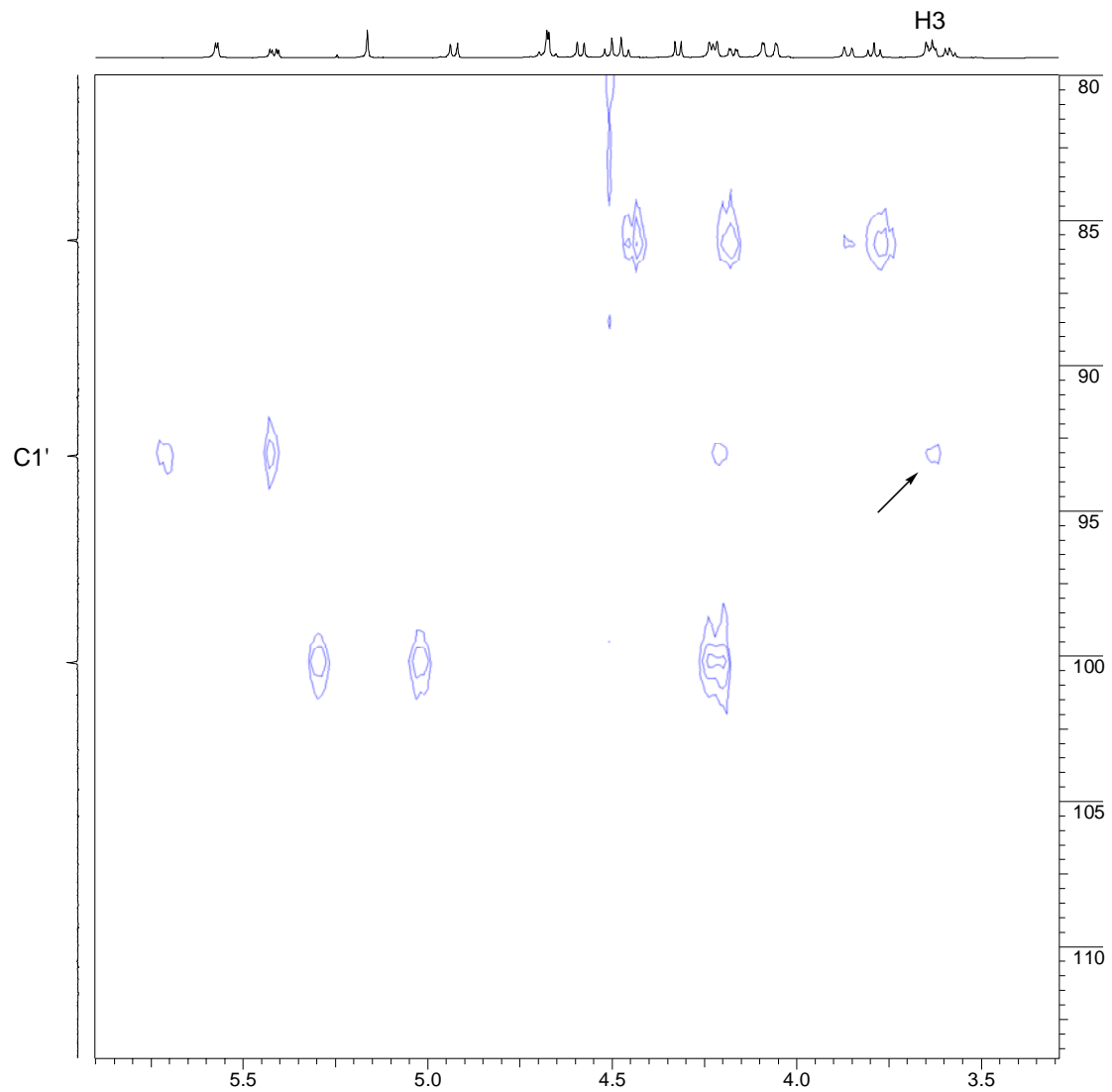
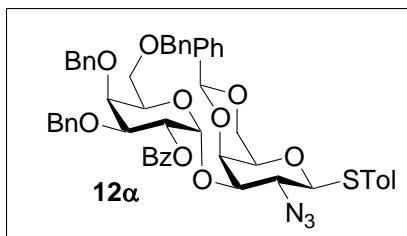
gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )



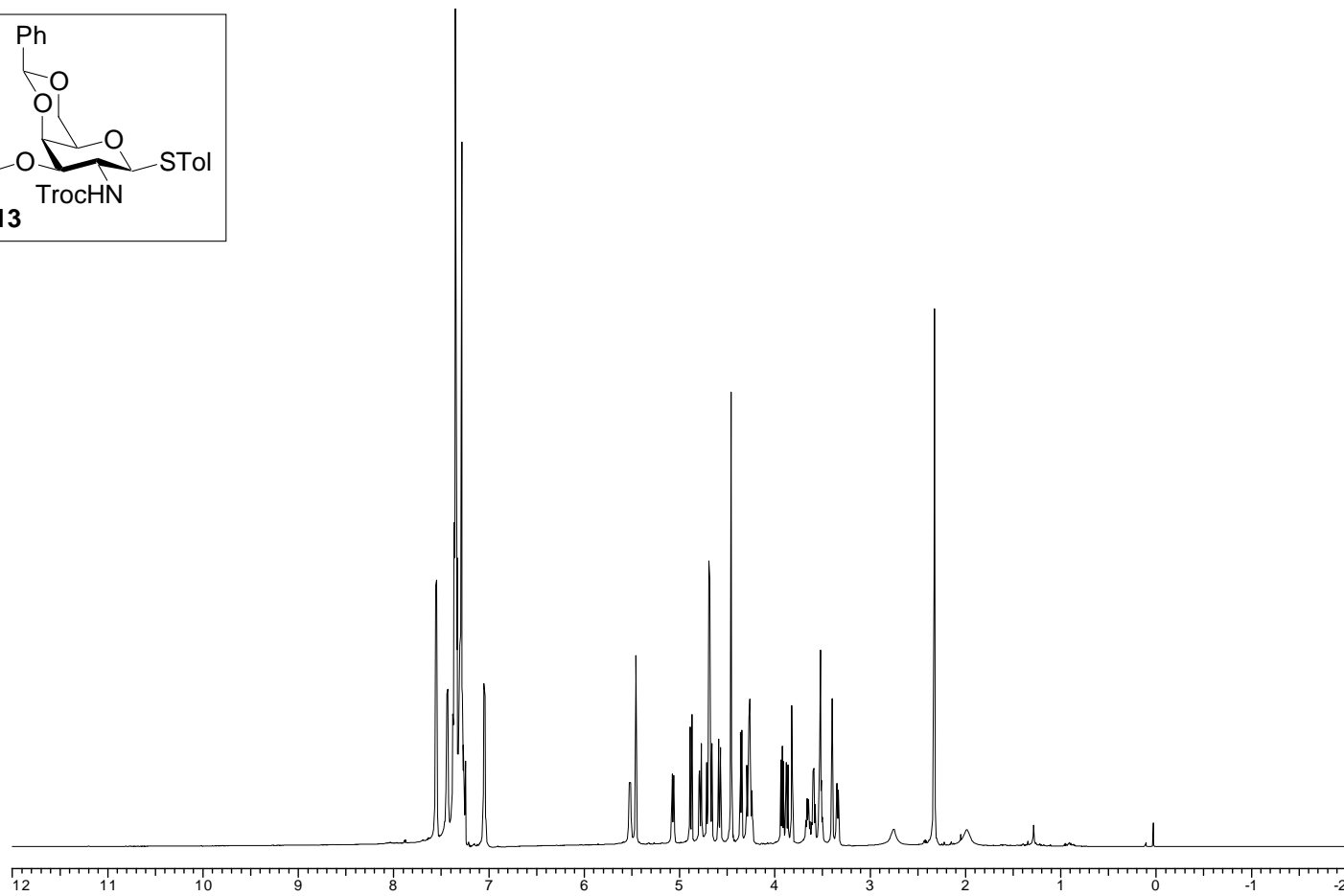
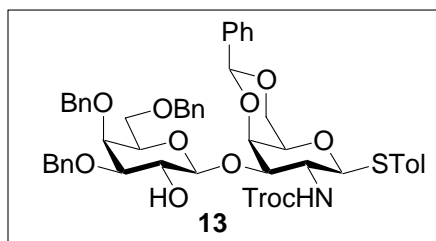
gHMBC (600 MHz, CDCl<sub>3</sub>)



gHMBC (600 MHz, CDCl<sub>3</sub>)

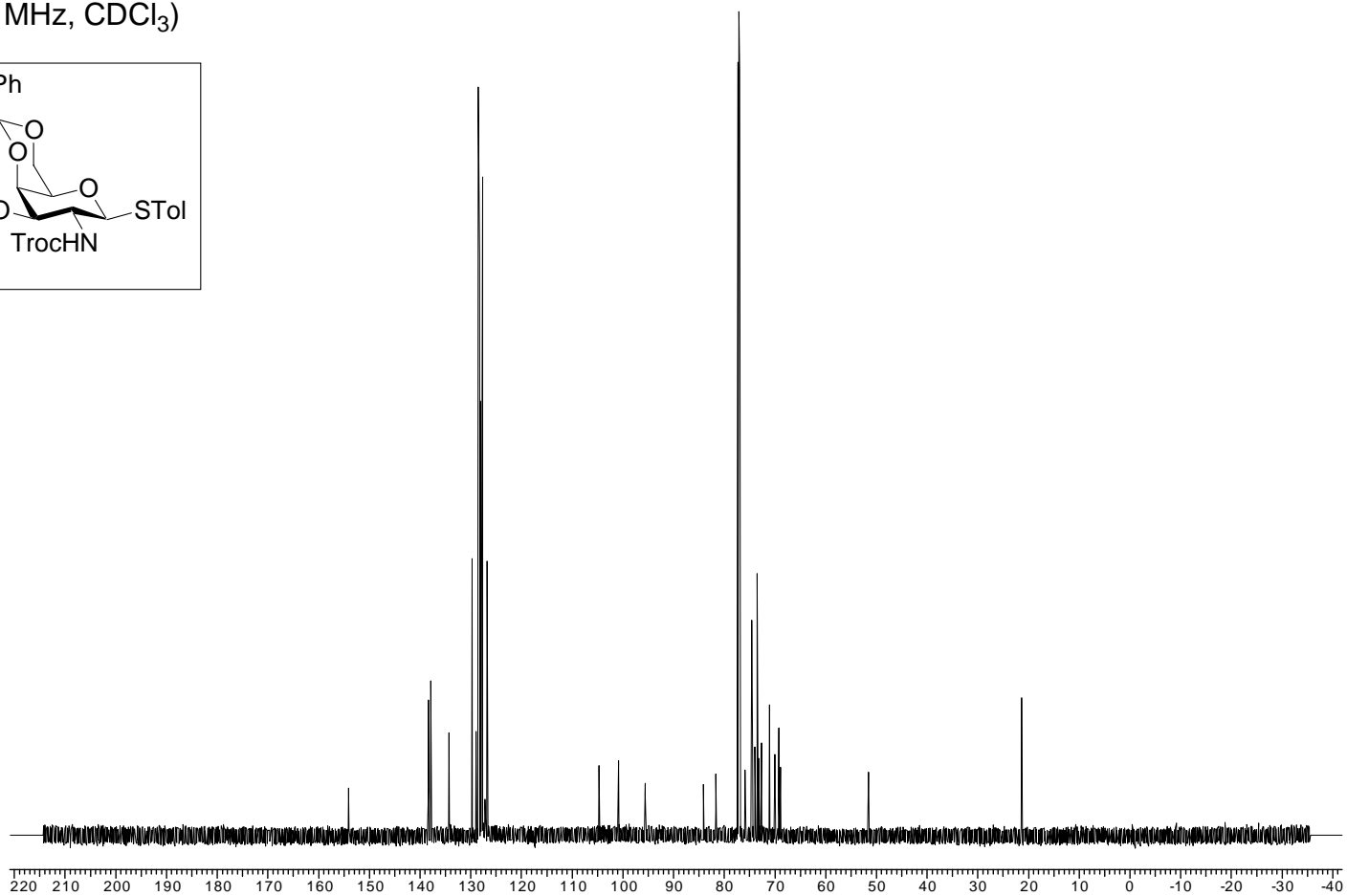
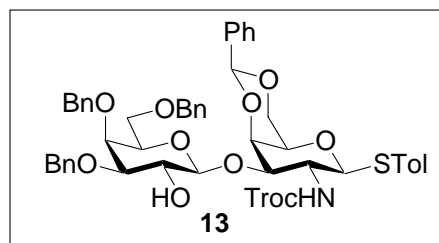


$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

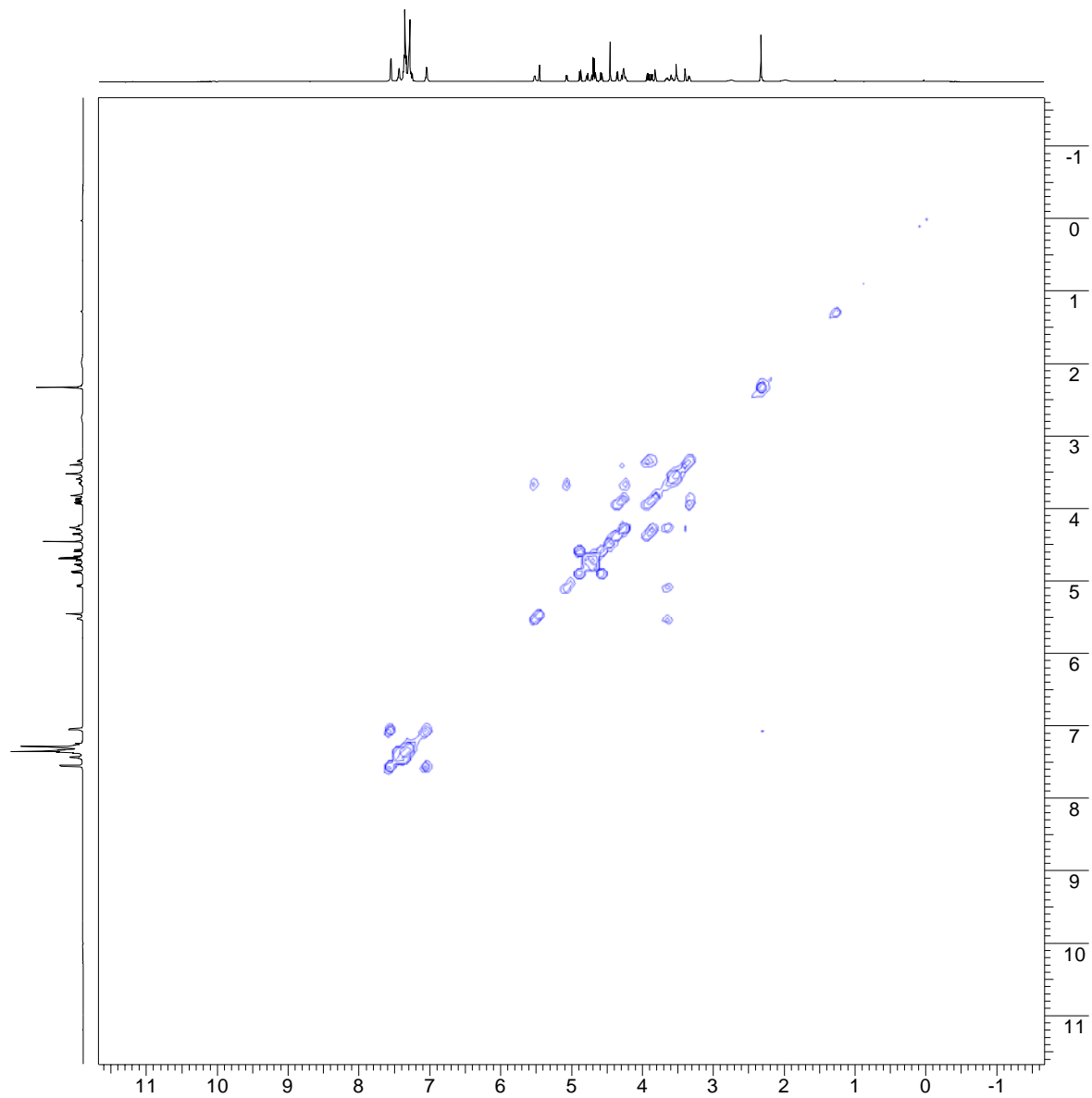
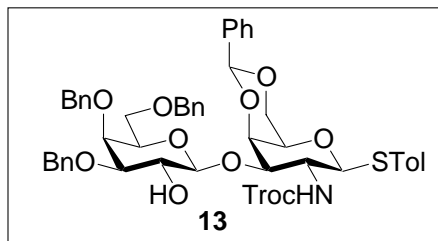




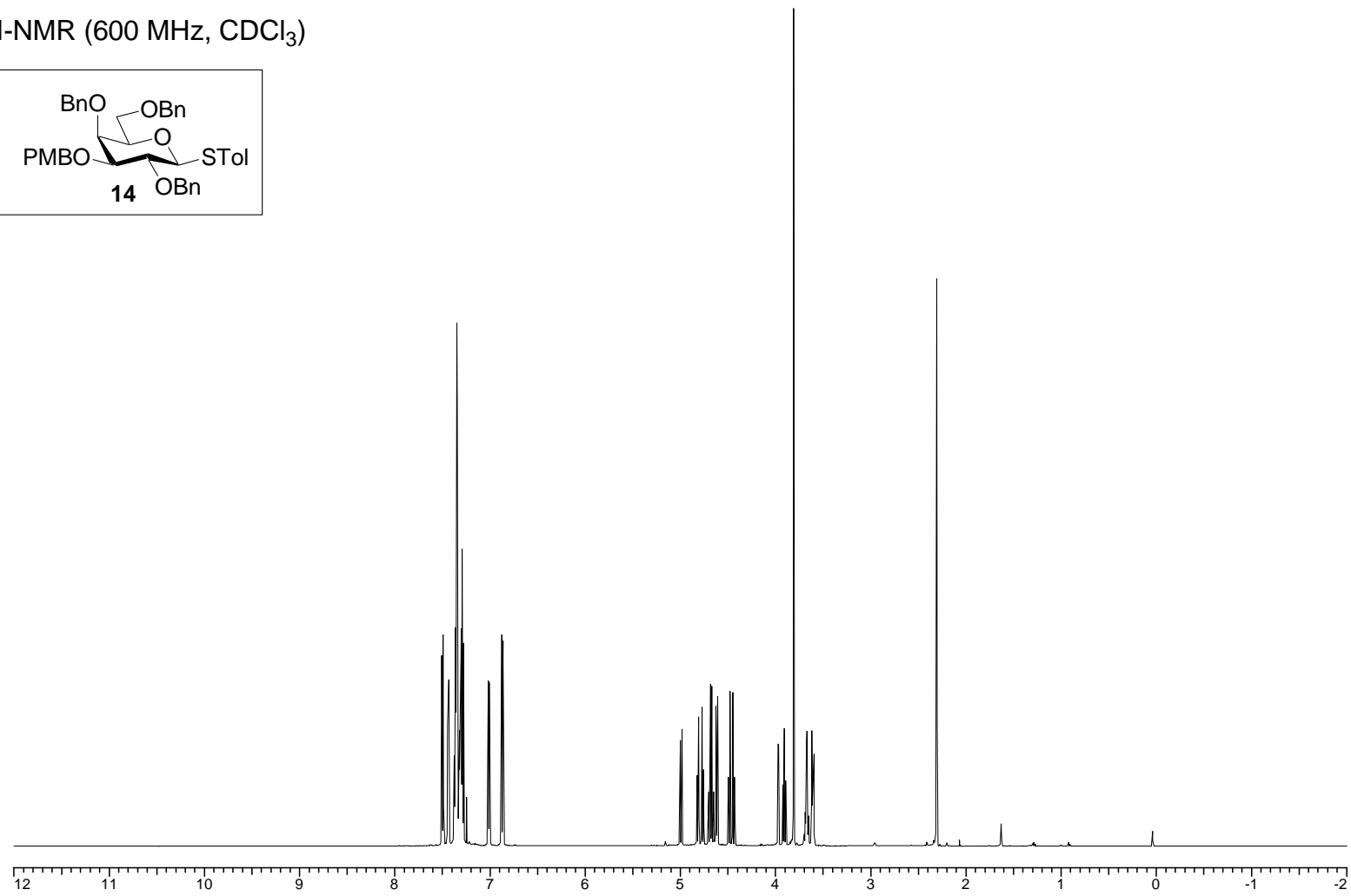
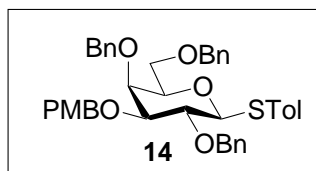
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



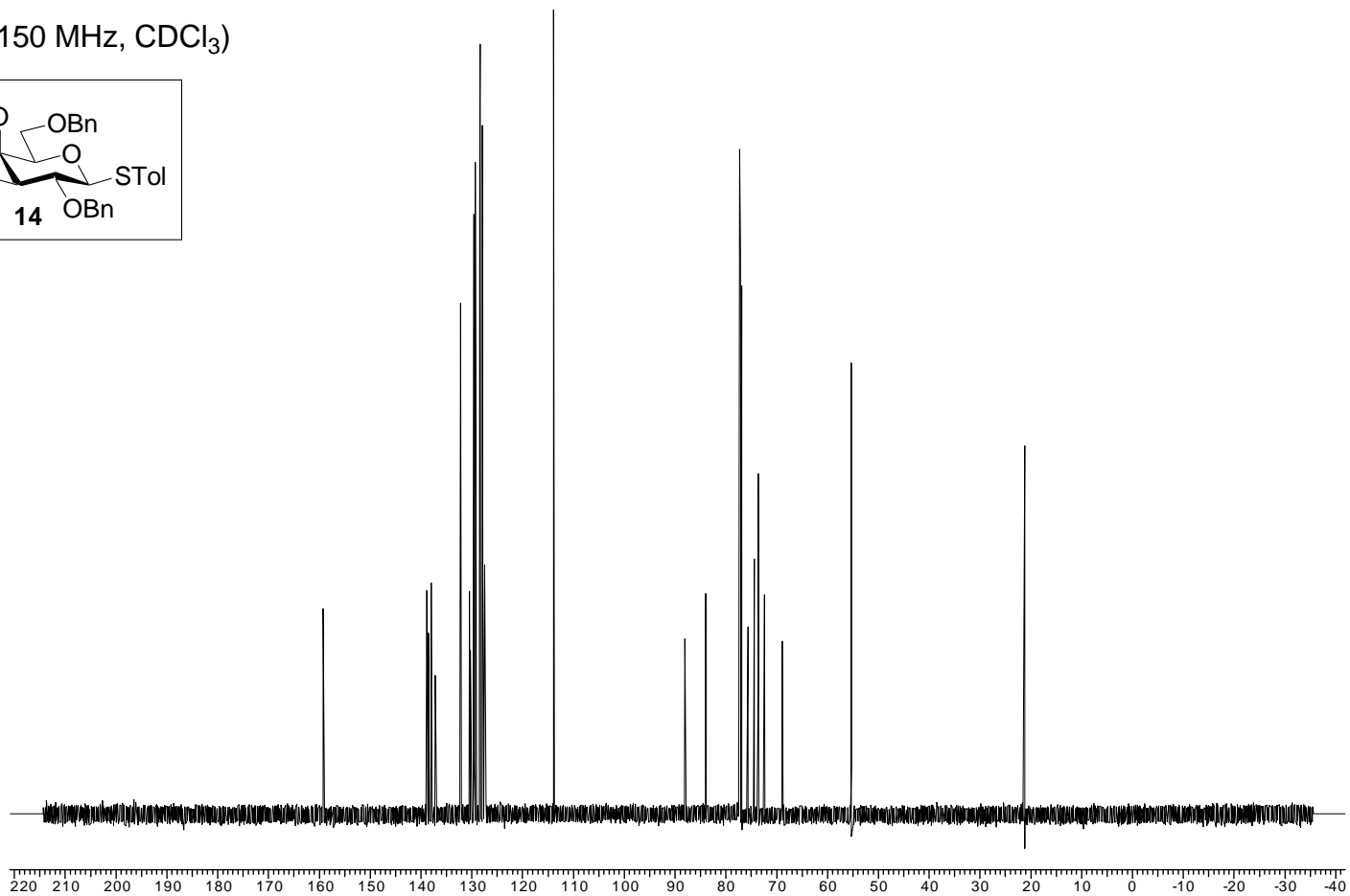
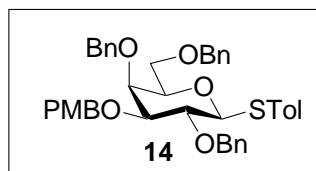
gCOSY (600 MHz, CDCl<sub>3</sub>)



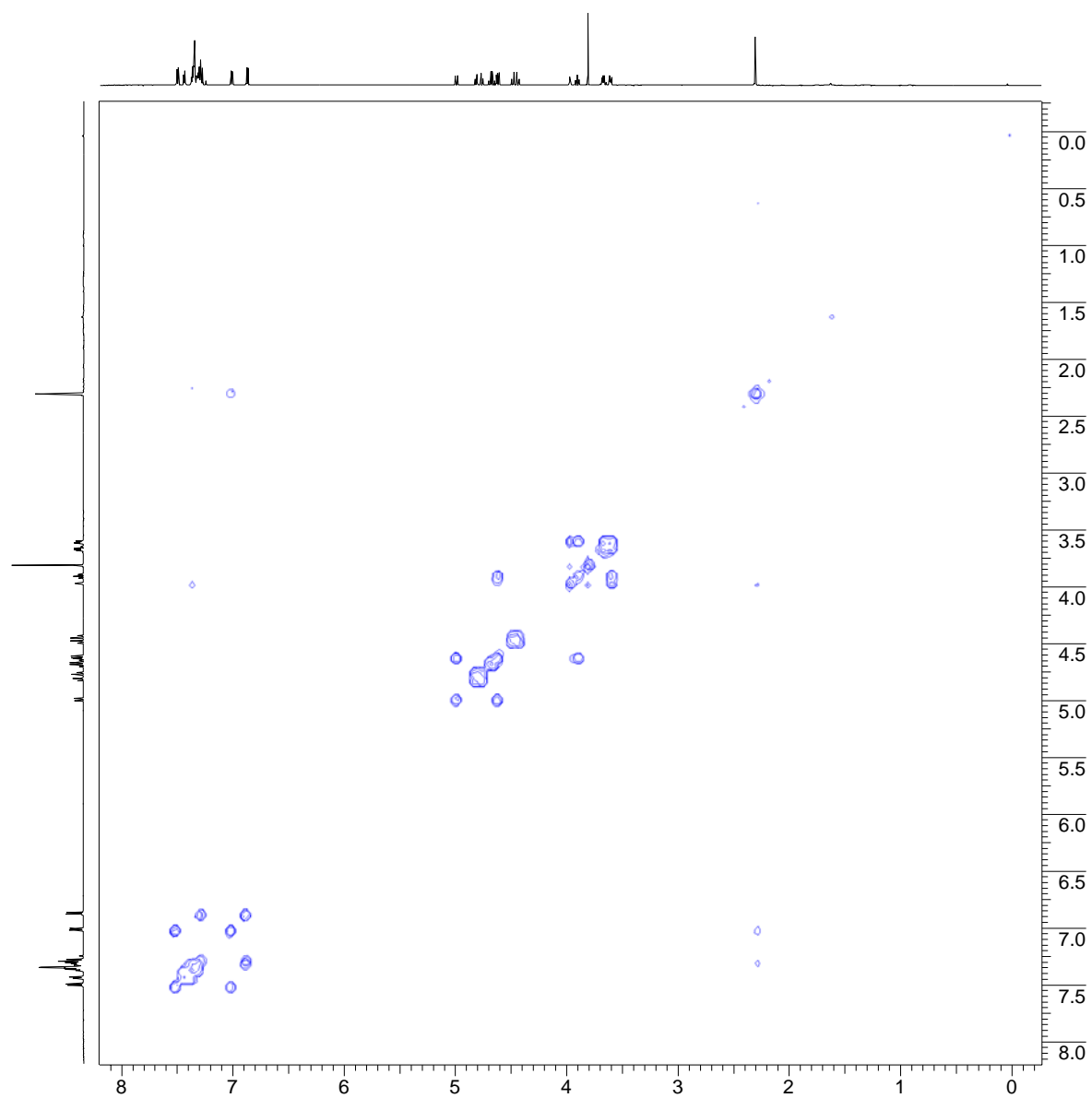
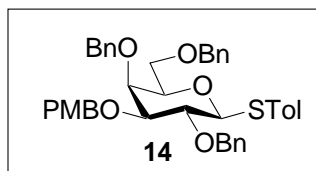
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



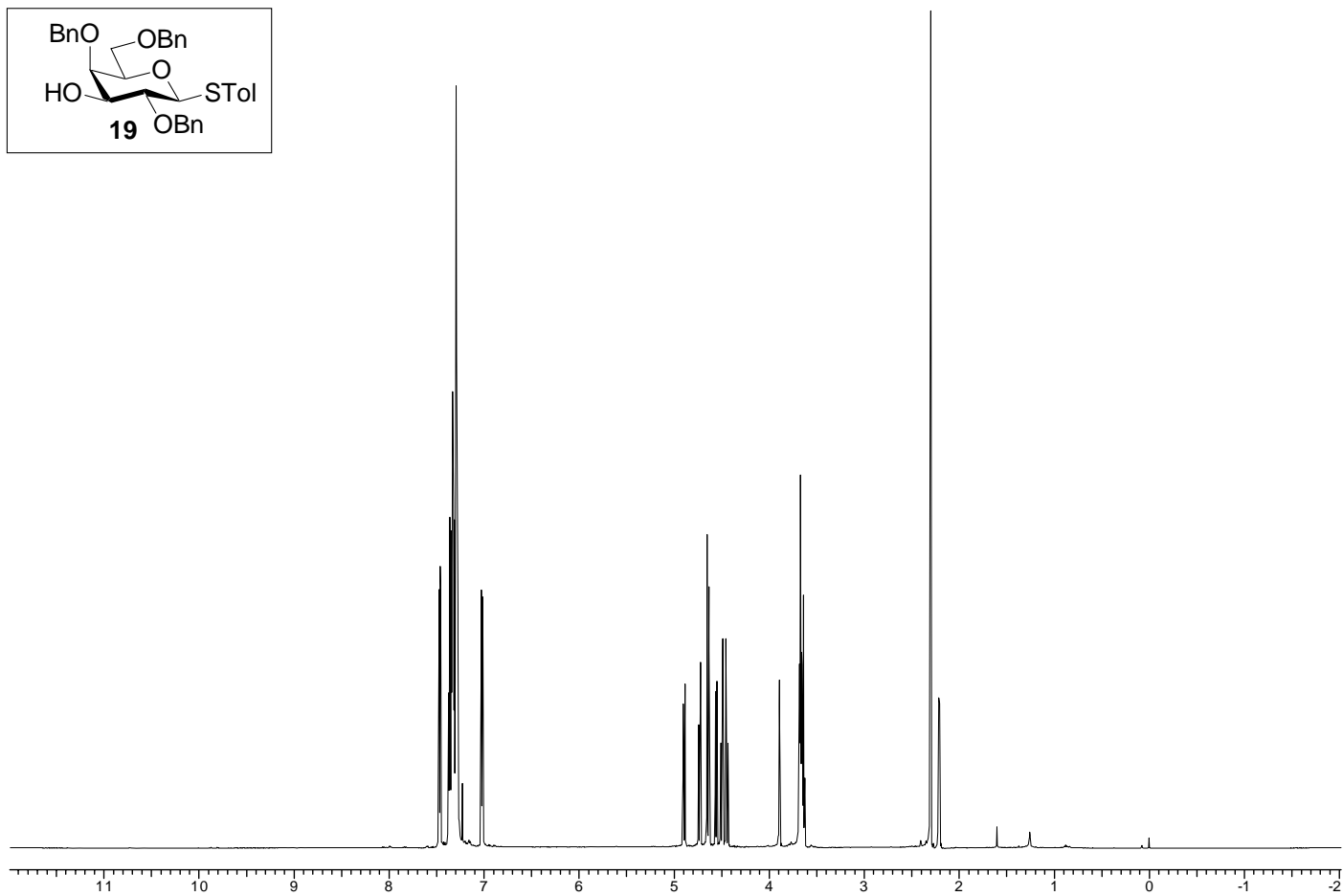
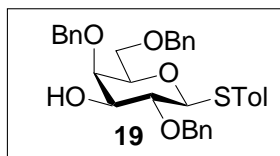
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



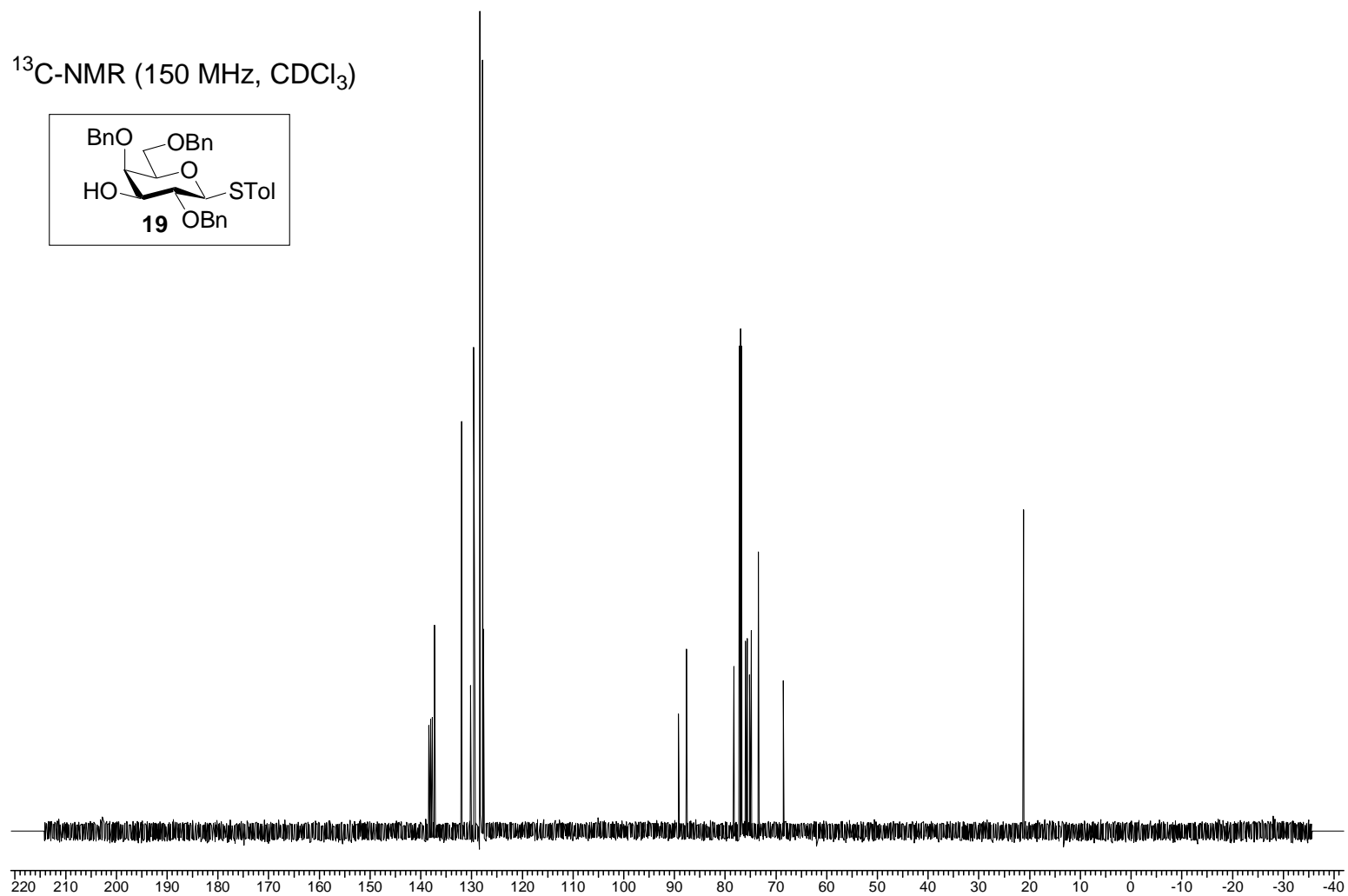
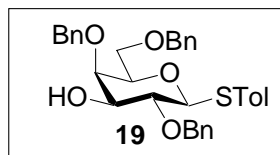
gCOSY (600 MHz, CDCl<sub>3</sub>)



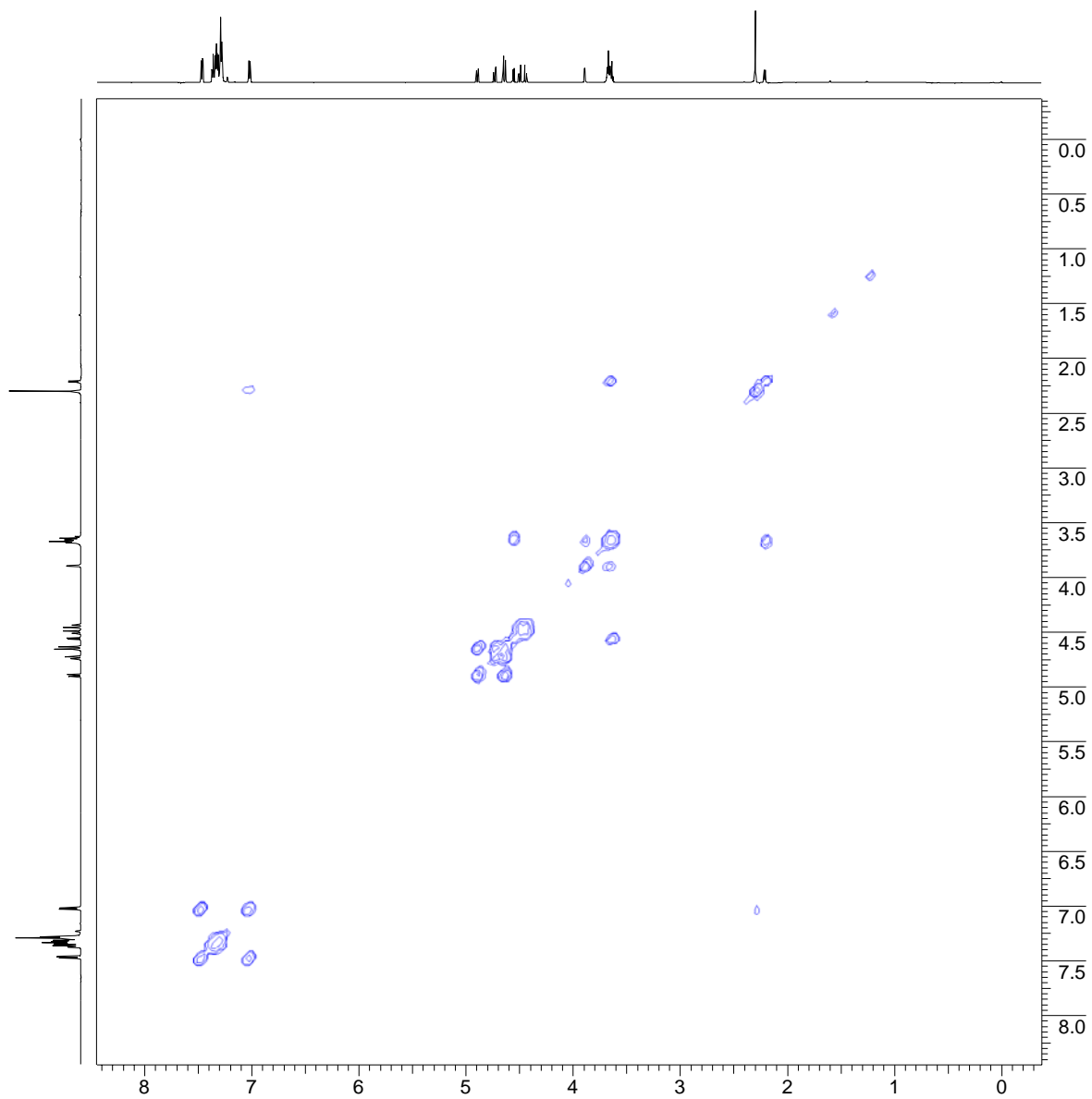
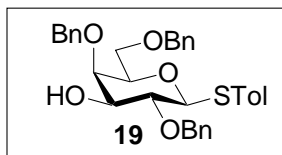
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )

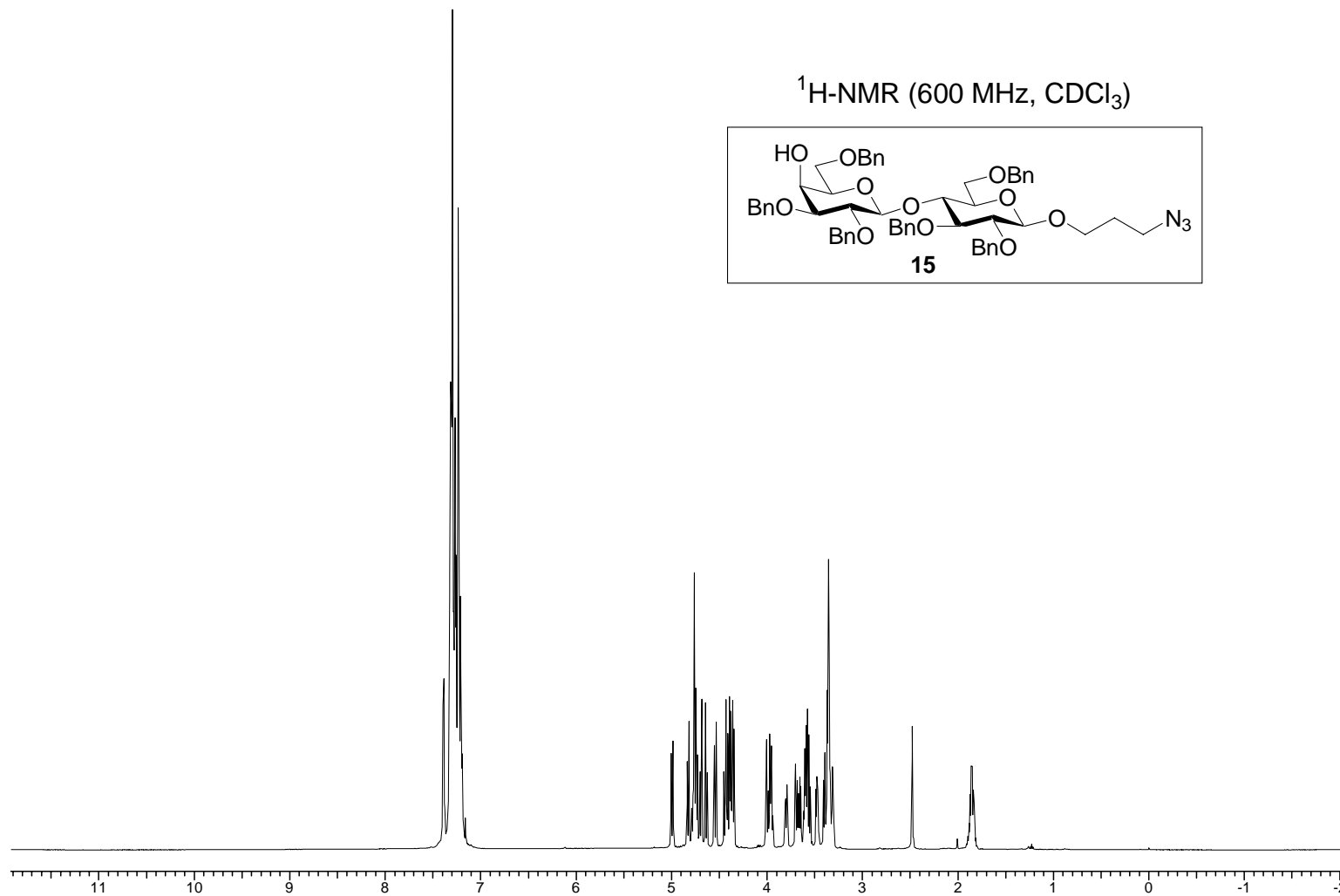
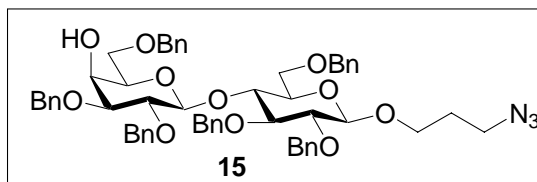


gCOSY (600 MHz, CDCl<sub>3</sub>)

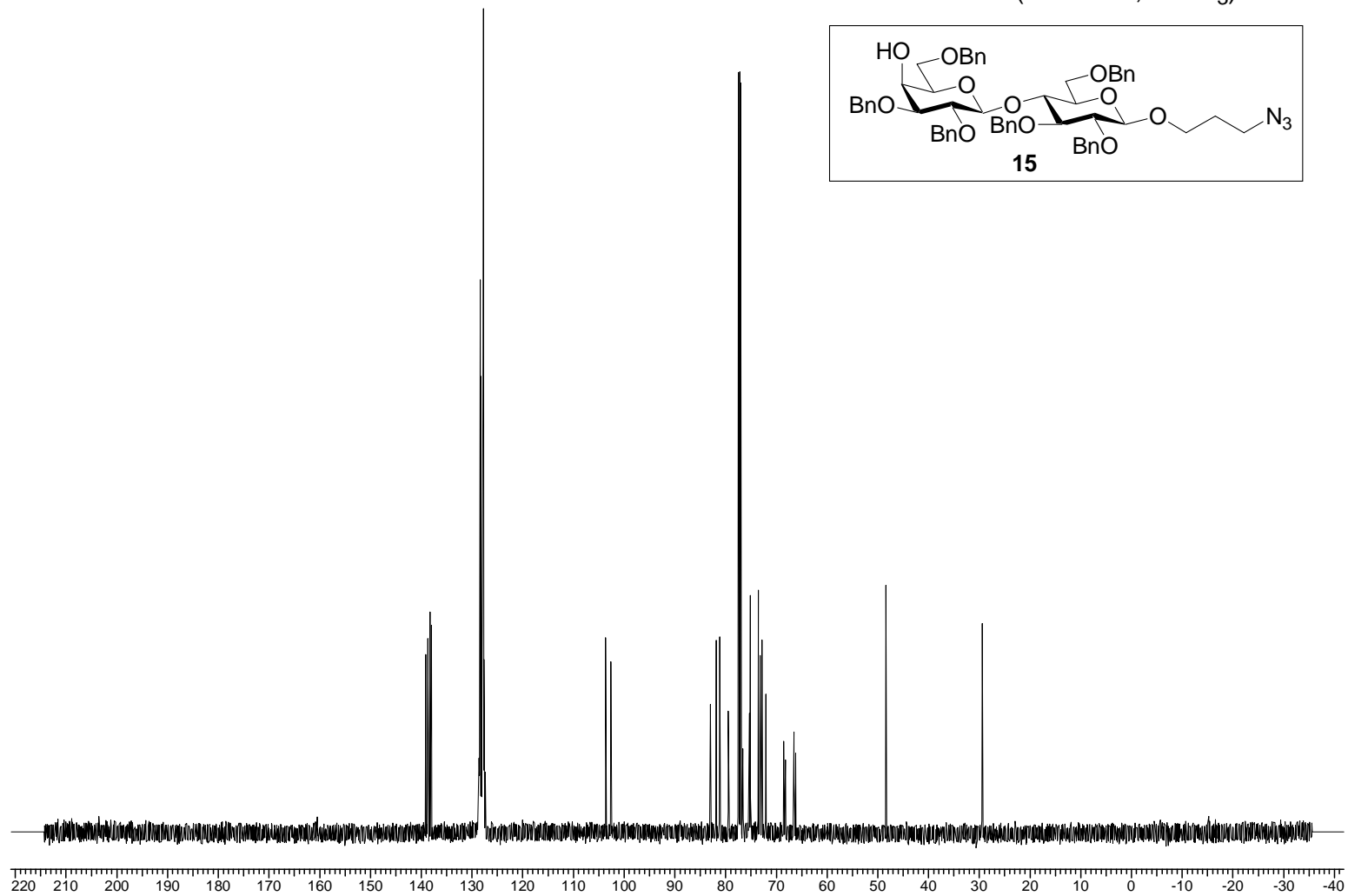
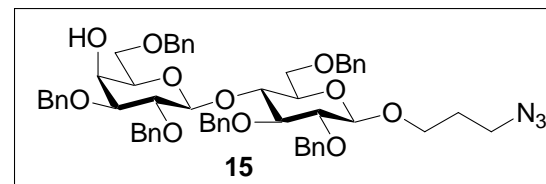




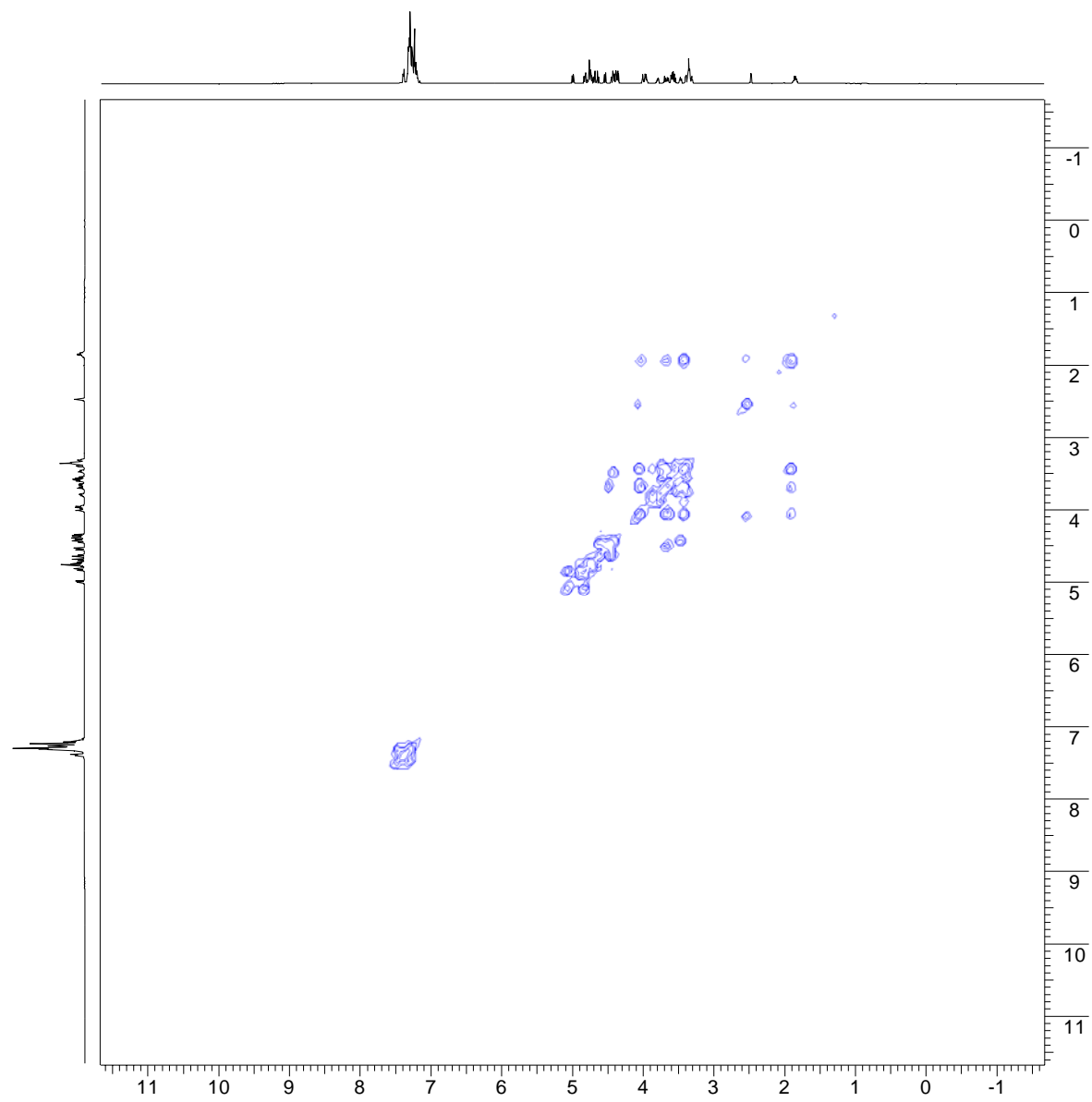
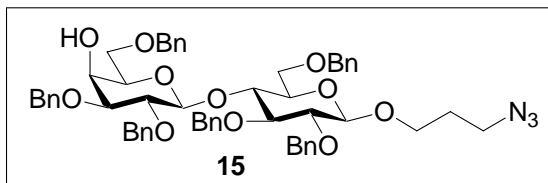
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



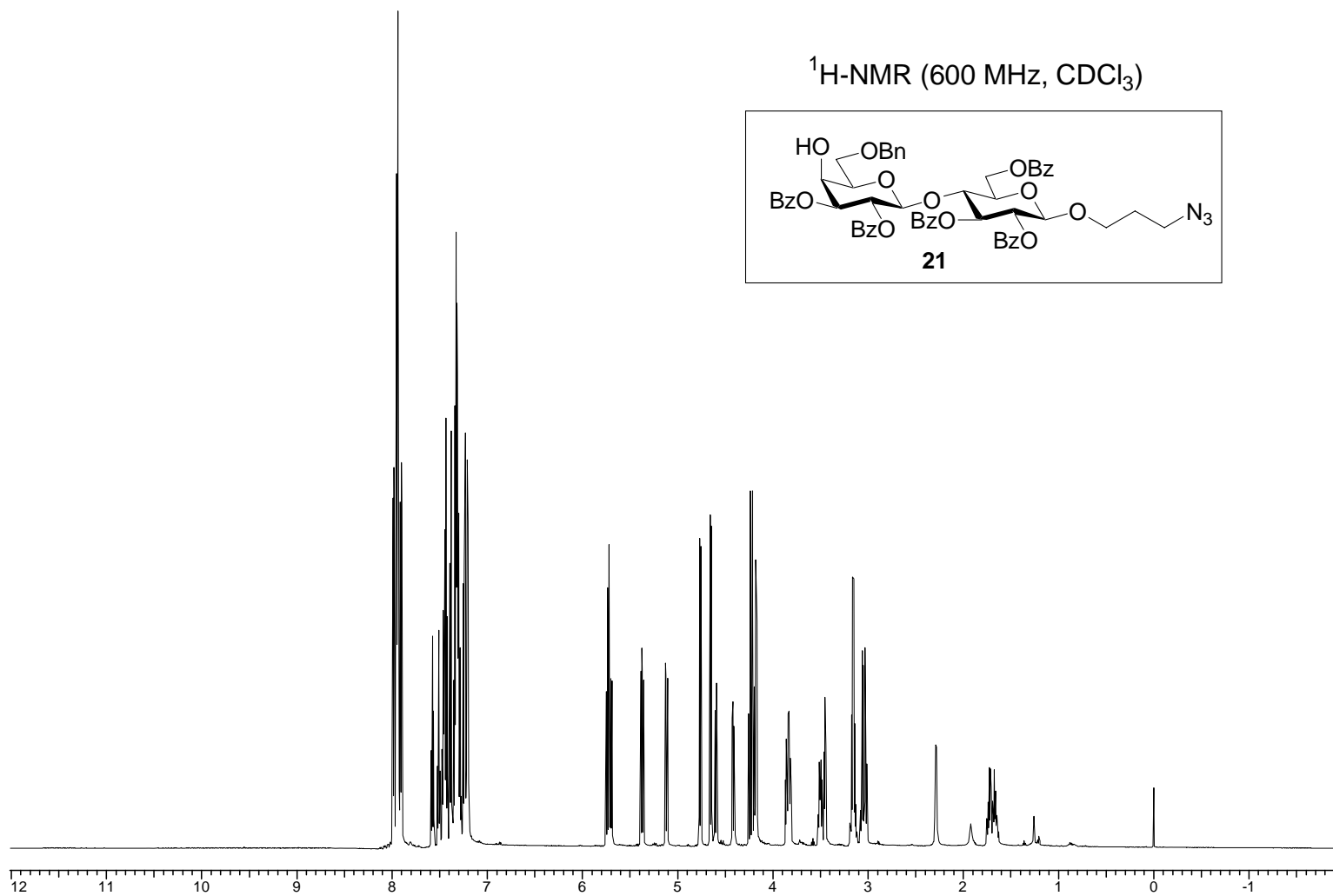
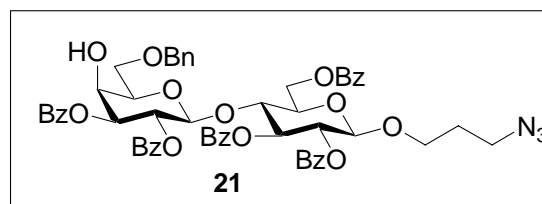
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



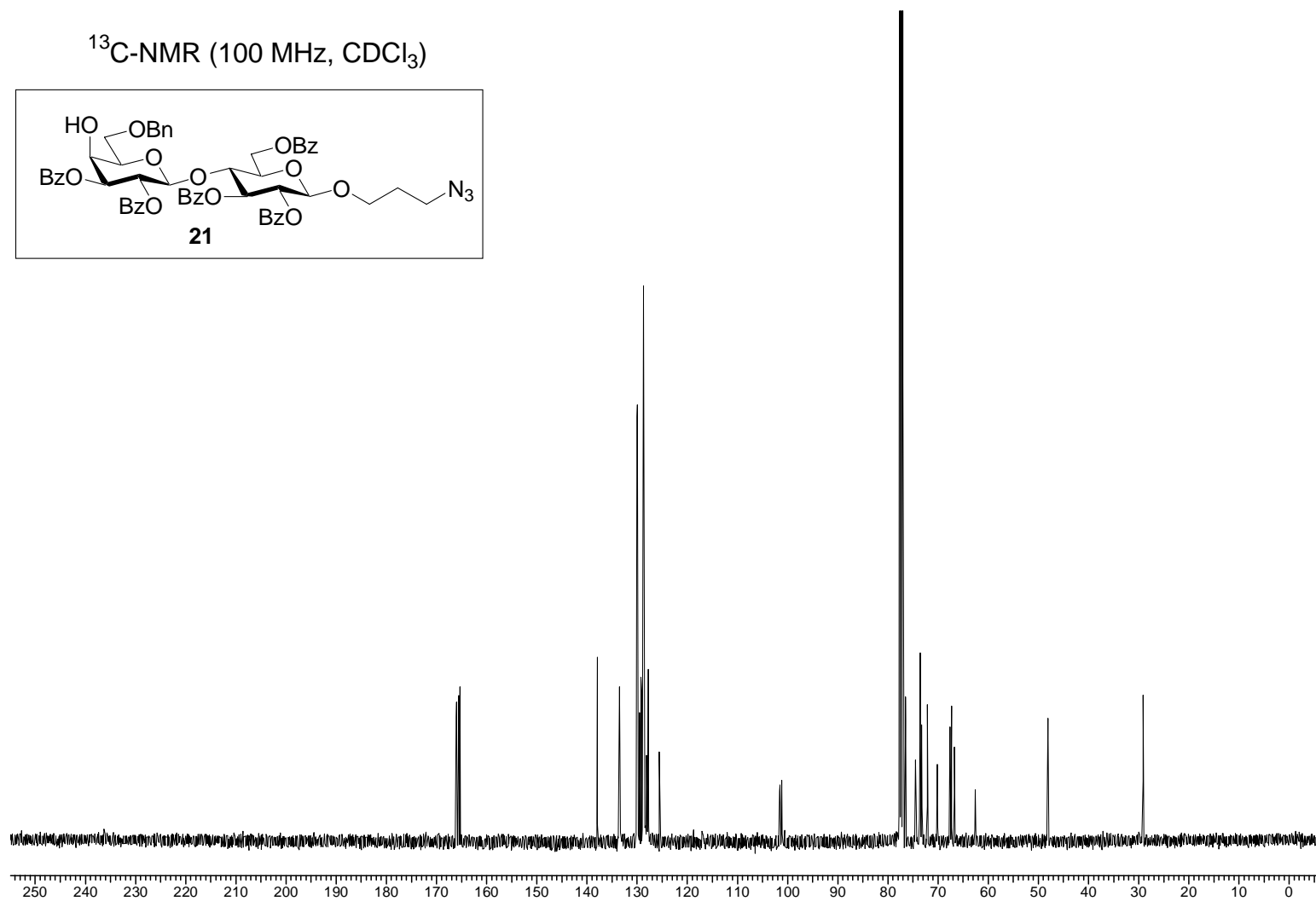
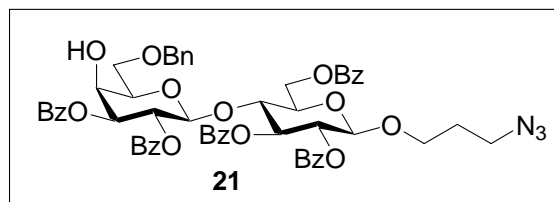
gCOSY (600 MHz, CDCl<sub>3</sub>)



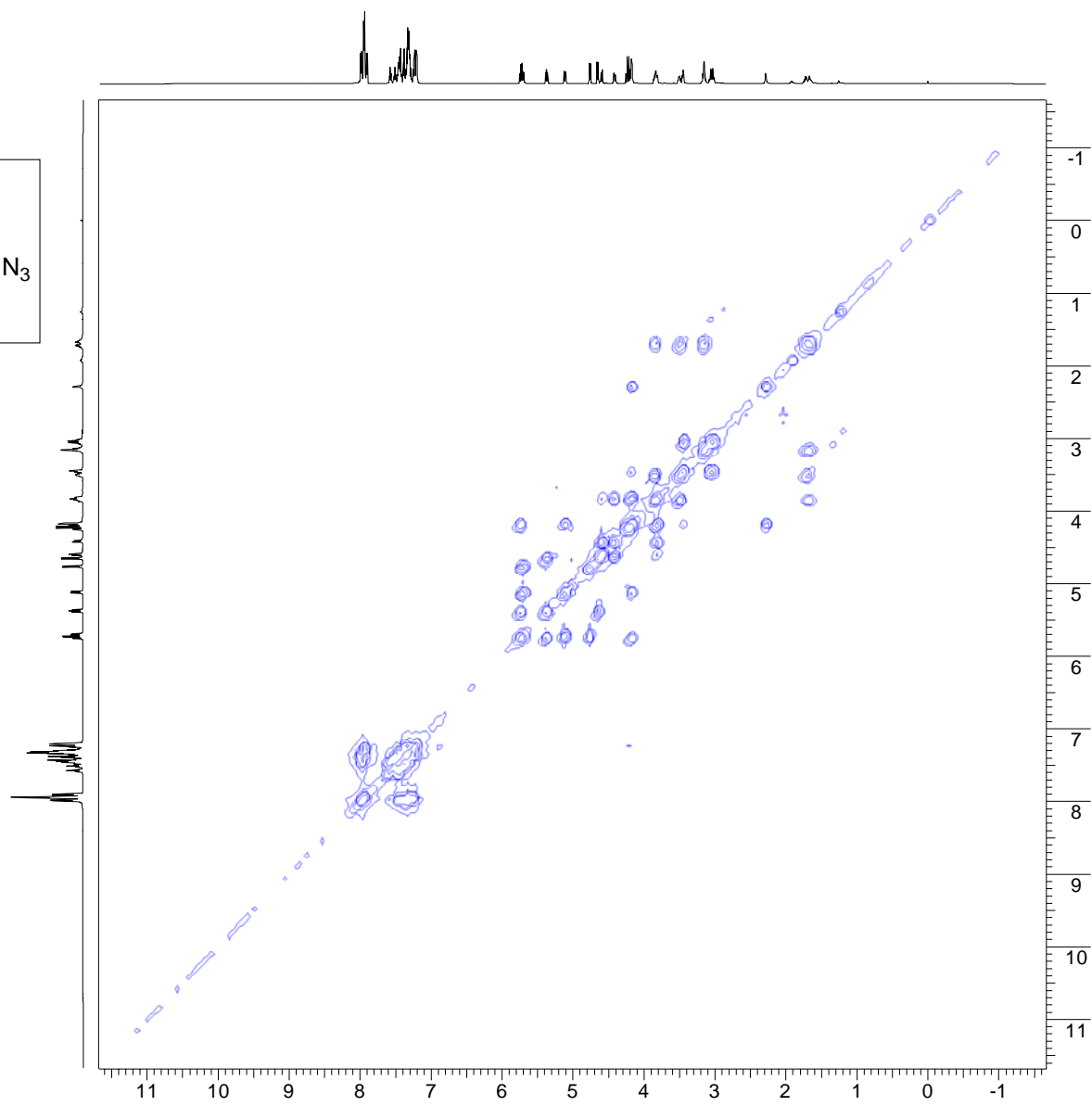
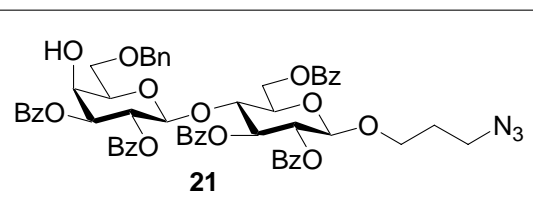
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



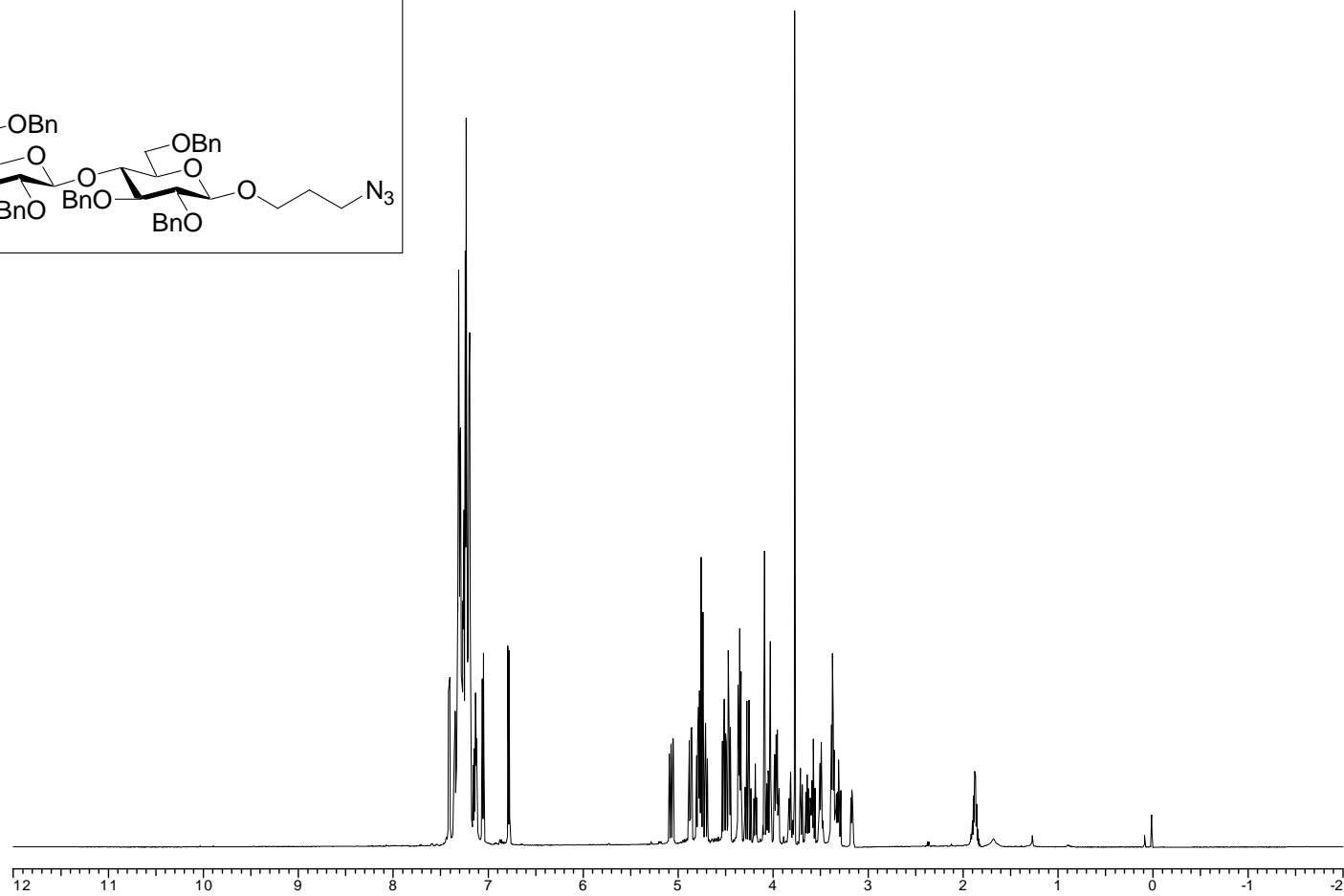
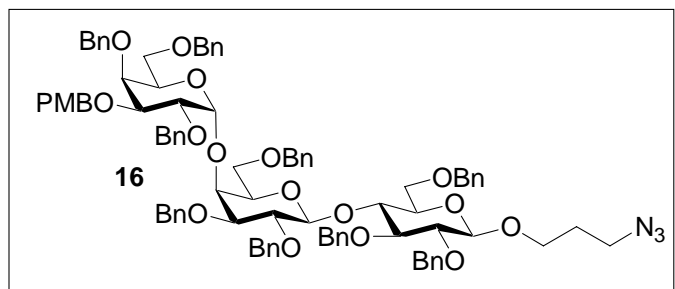
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )



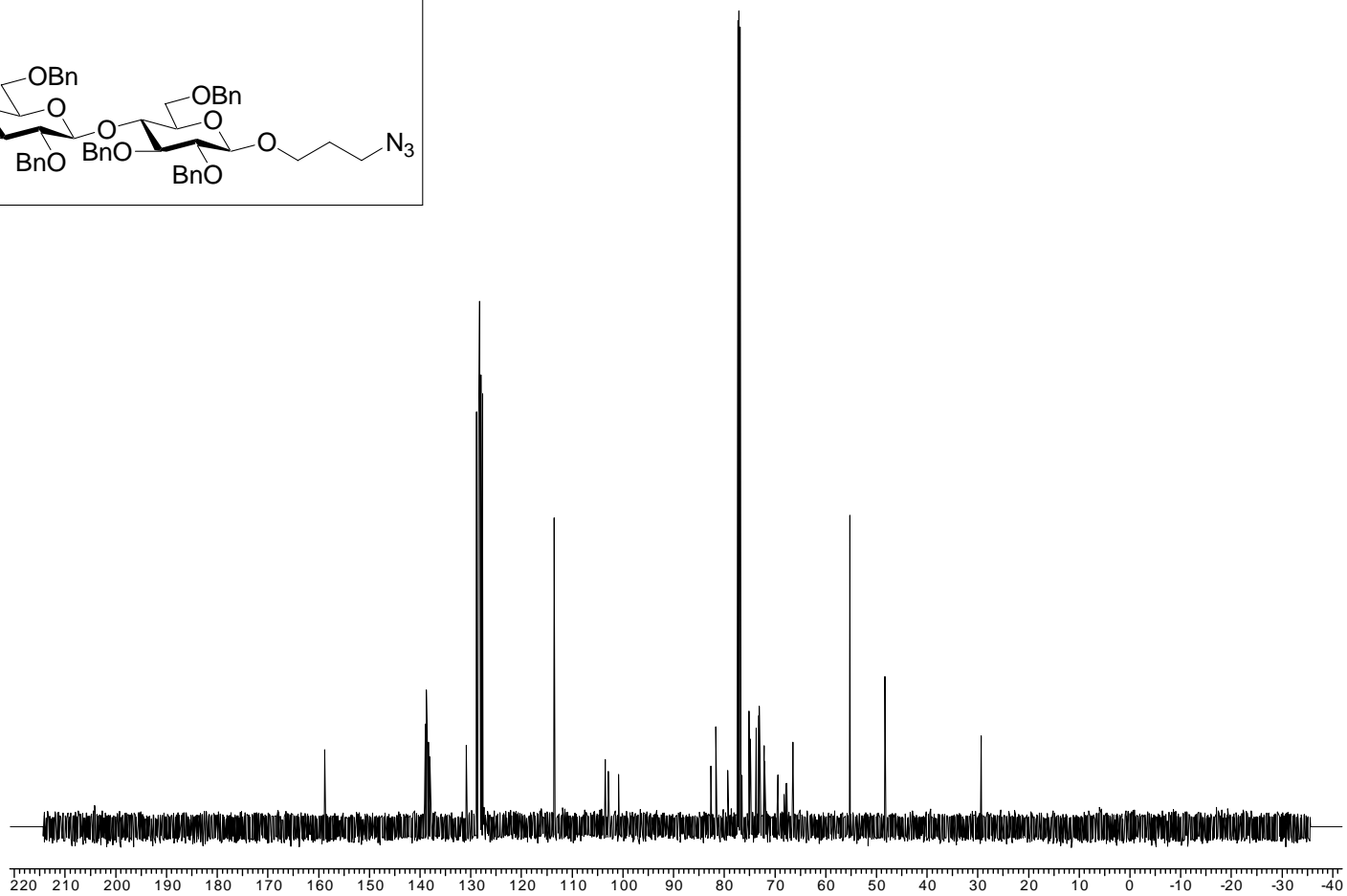
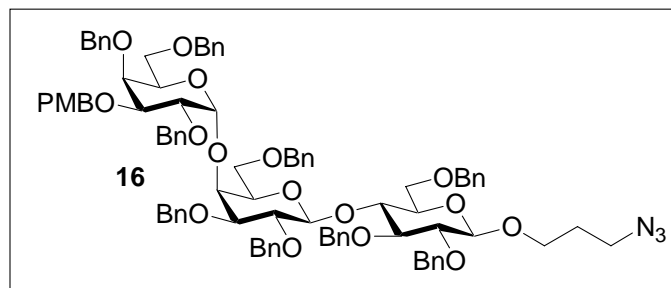
gCOSY (600 MHz, CDCl<sub>3</sub>)



$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

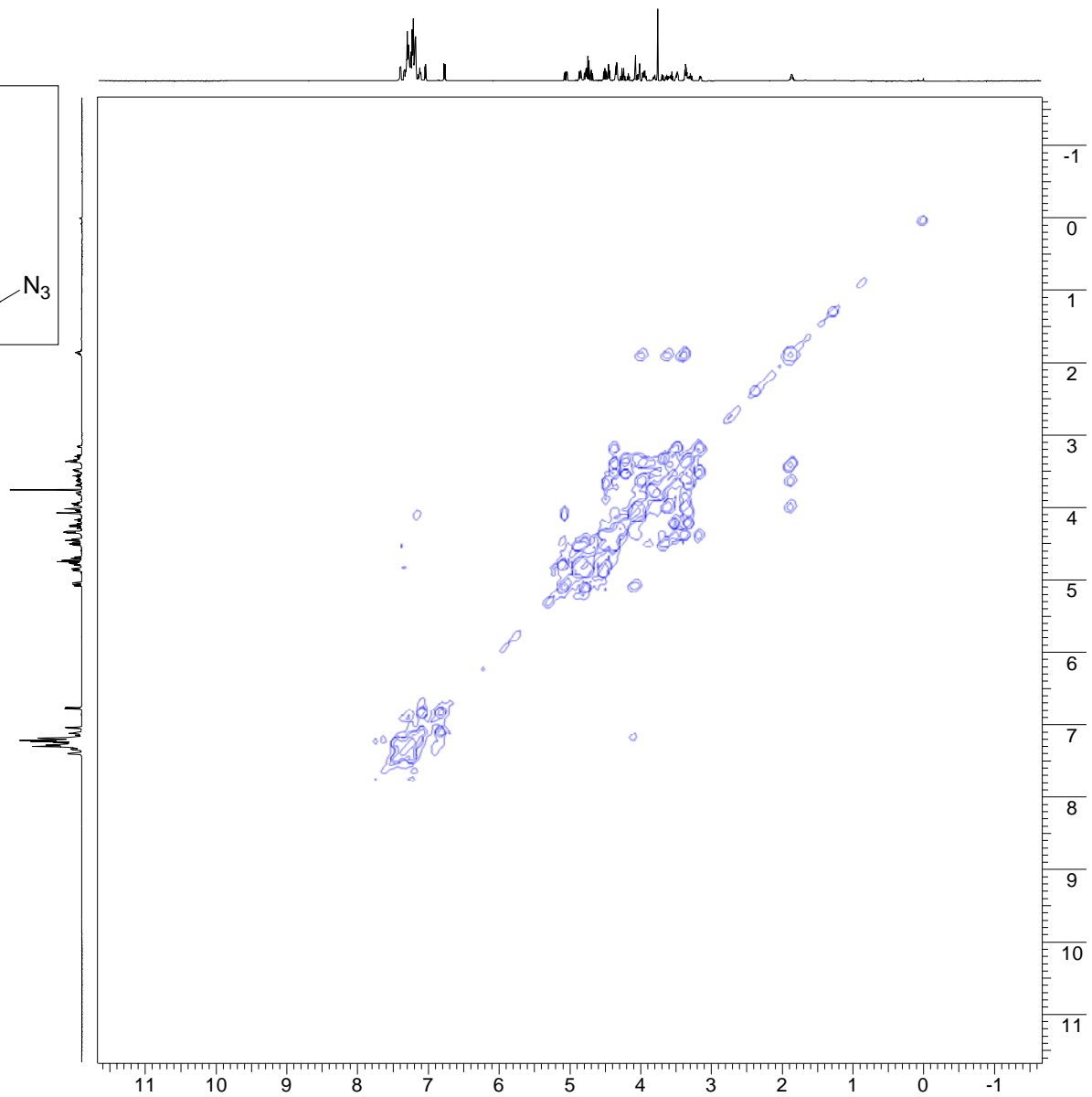
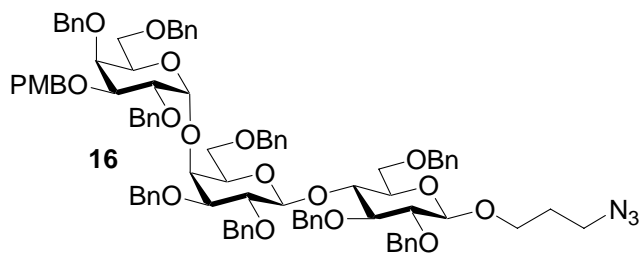


$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )

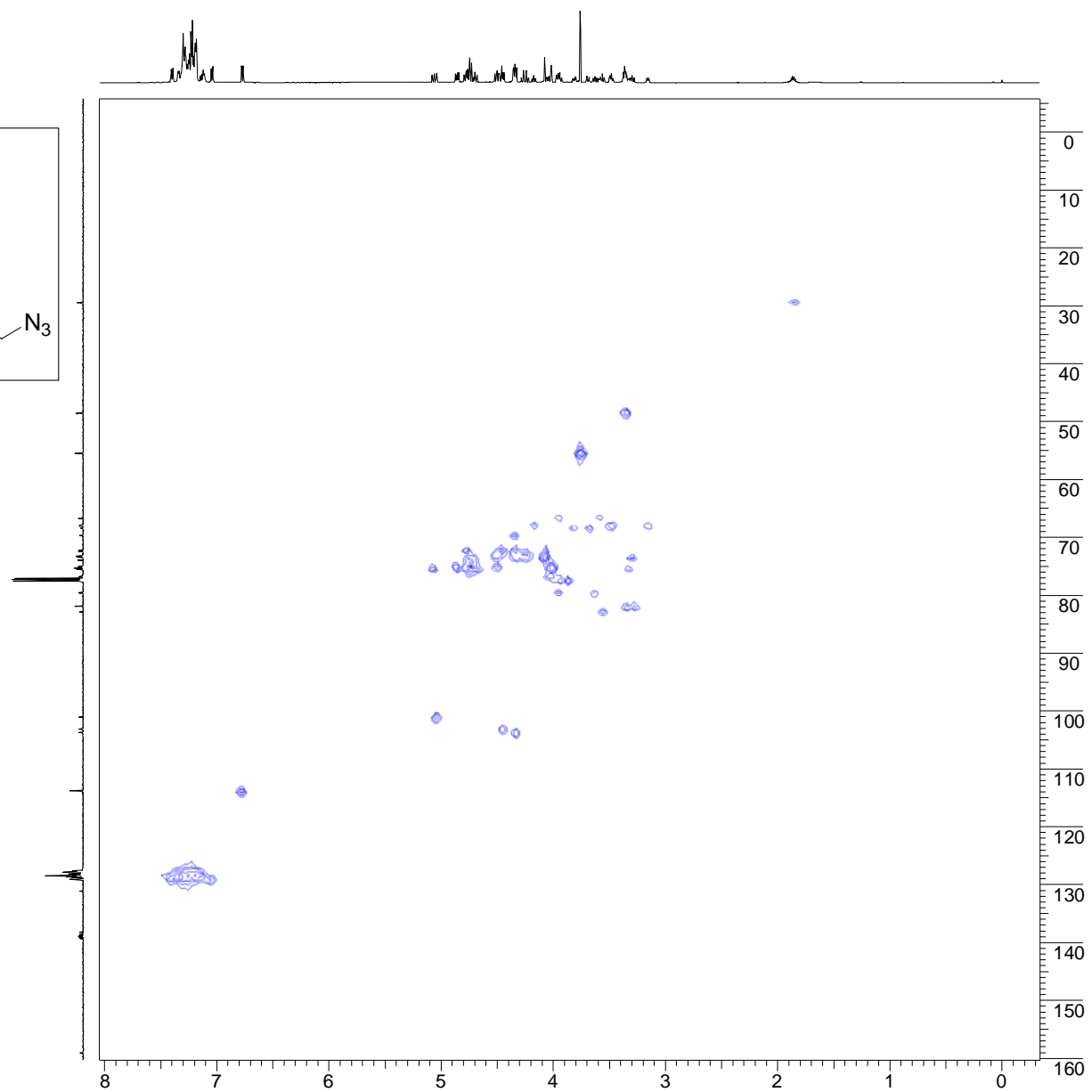
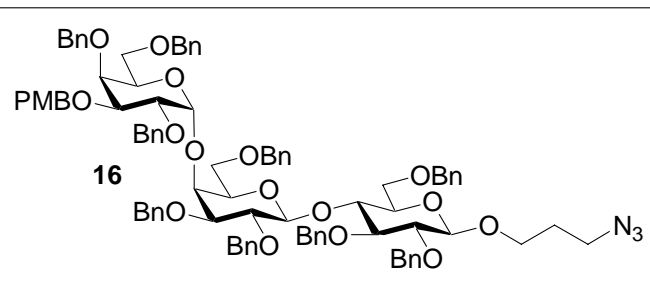




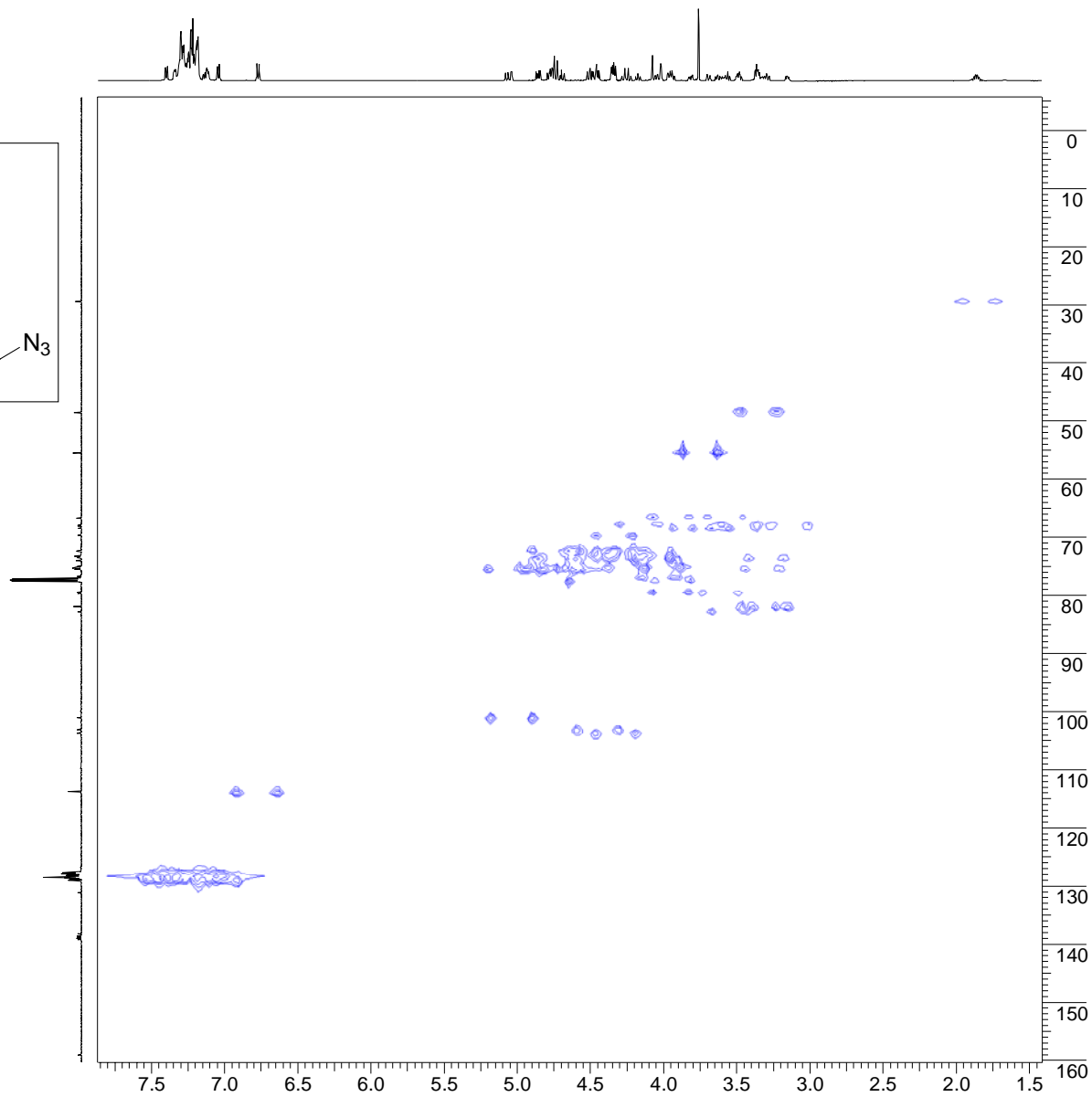
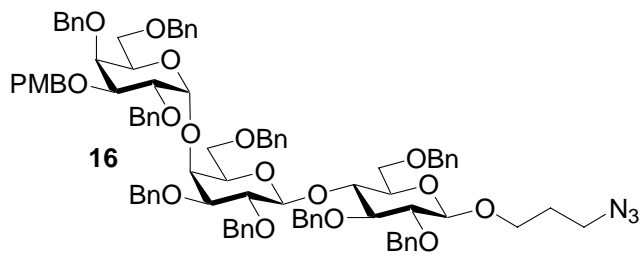
gCOSY (600 MHz, CDCl<sub>3</sub>)



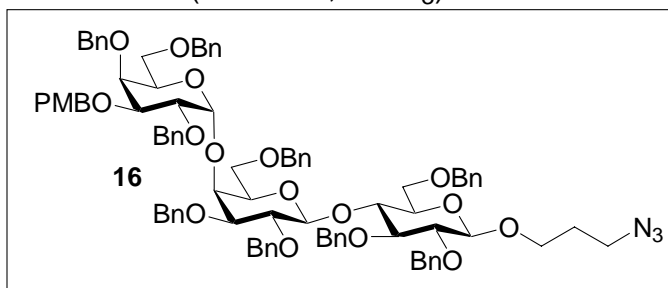
gHMQC (600 MHz, CDCl<sub>3</sub>)



gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )



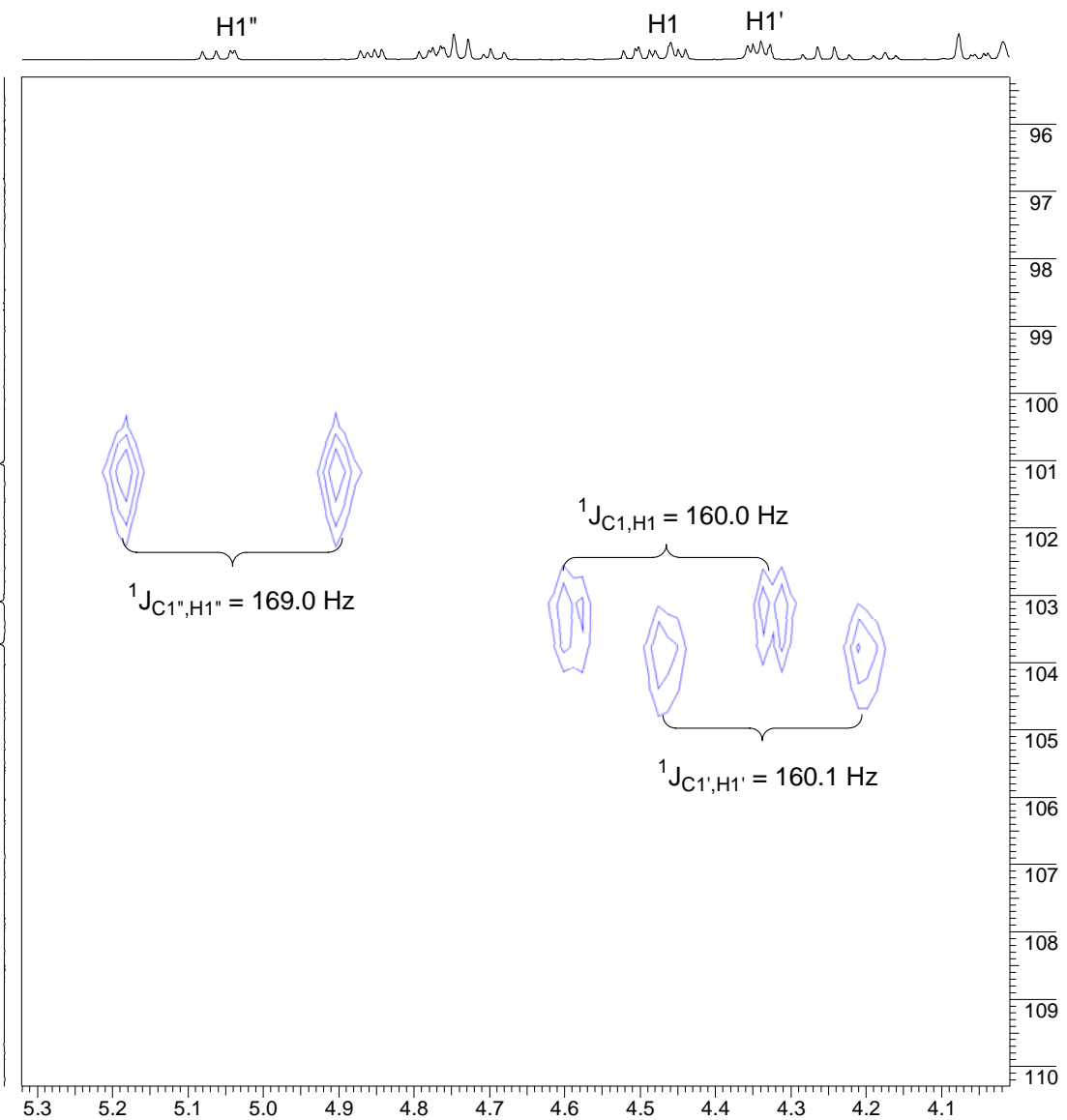
gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )



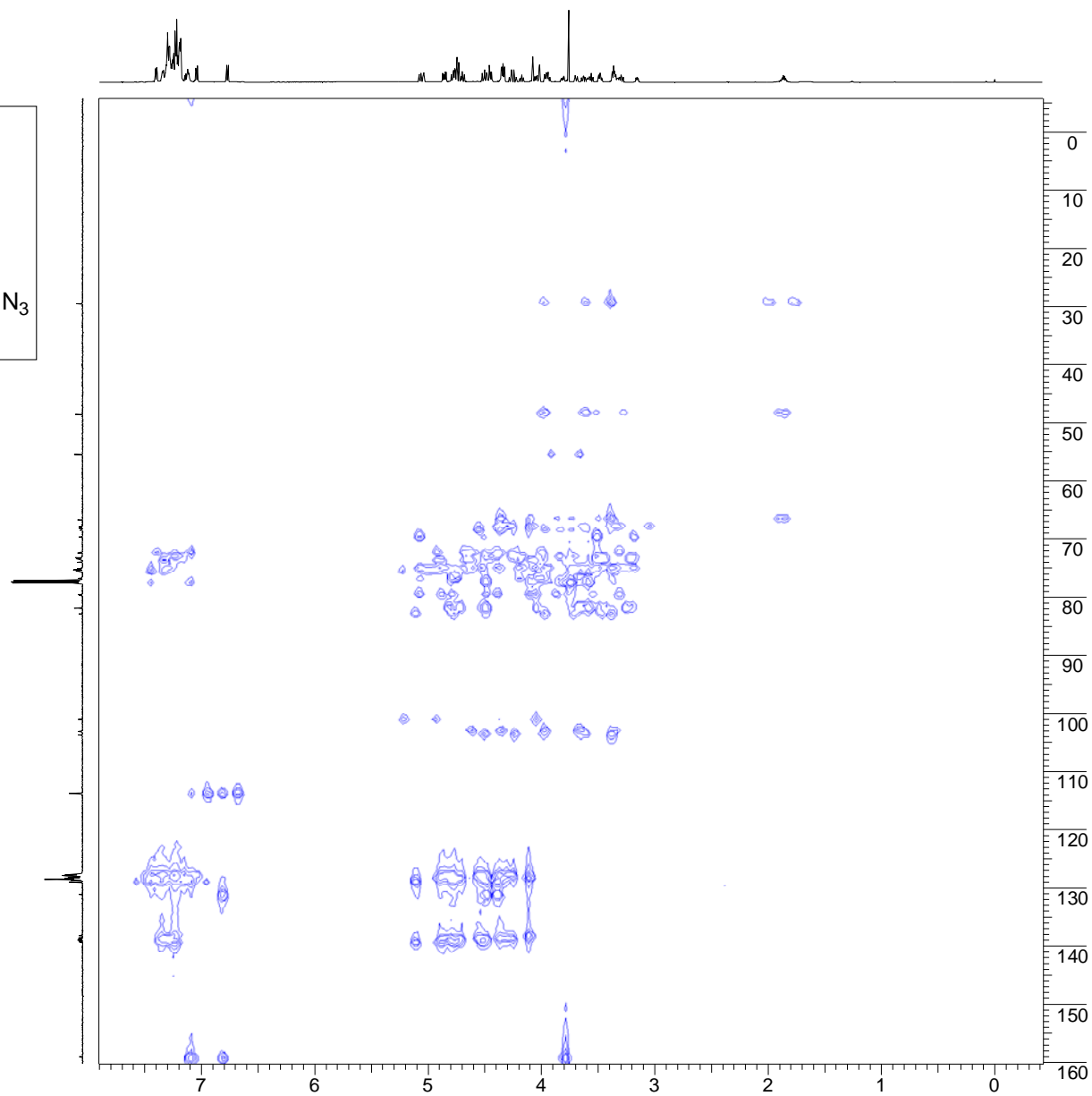
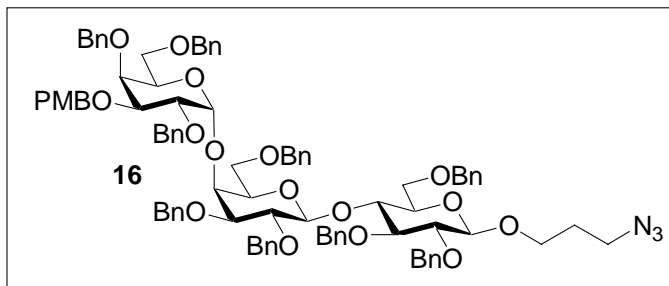
C1''

C1

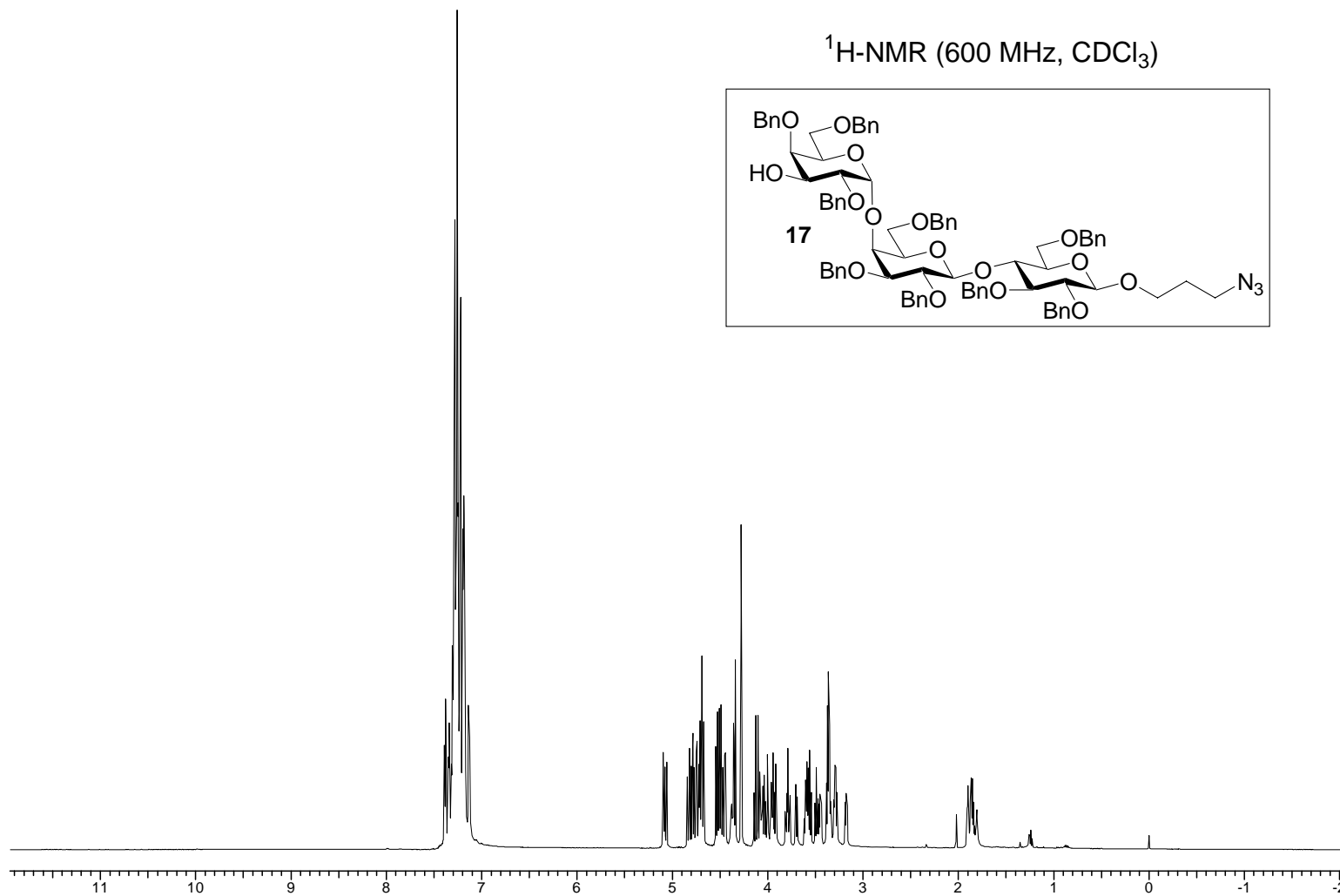
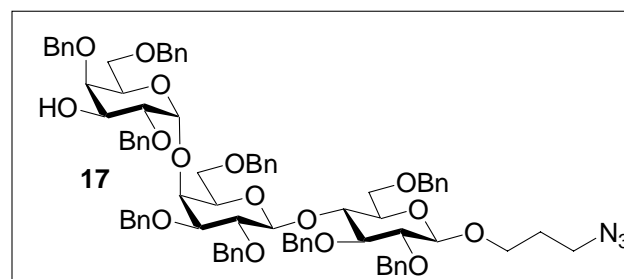
C1'



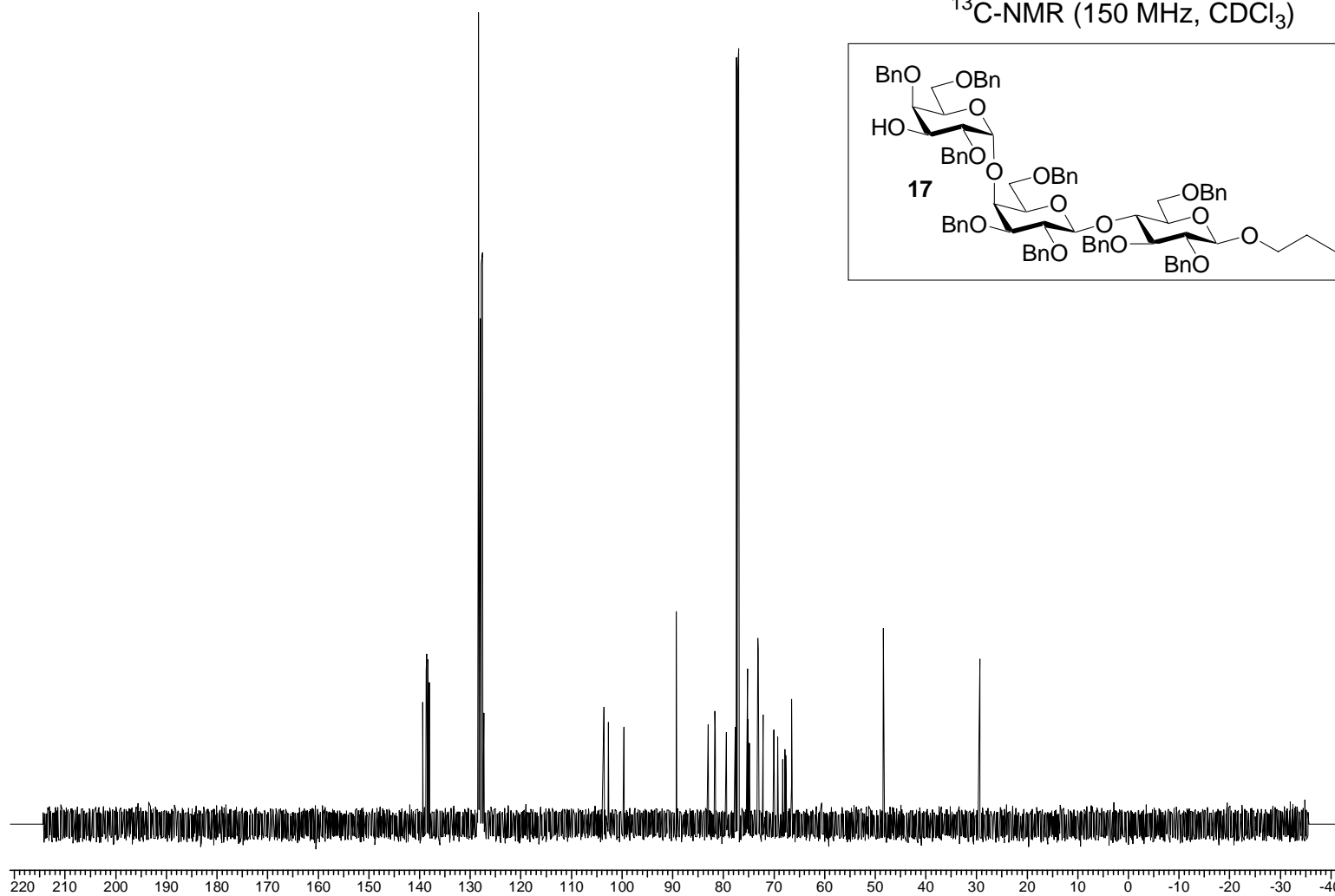
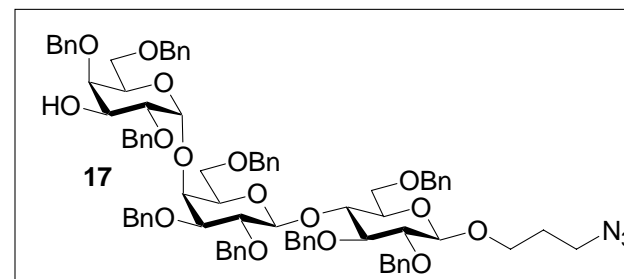
gHMBC (600 MHz, CDCl<sub>3</sub>)



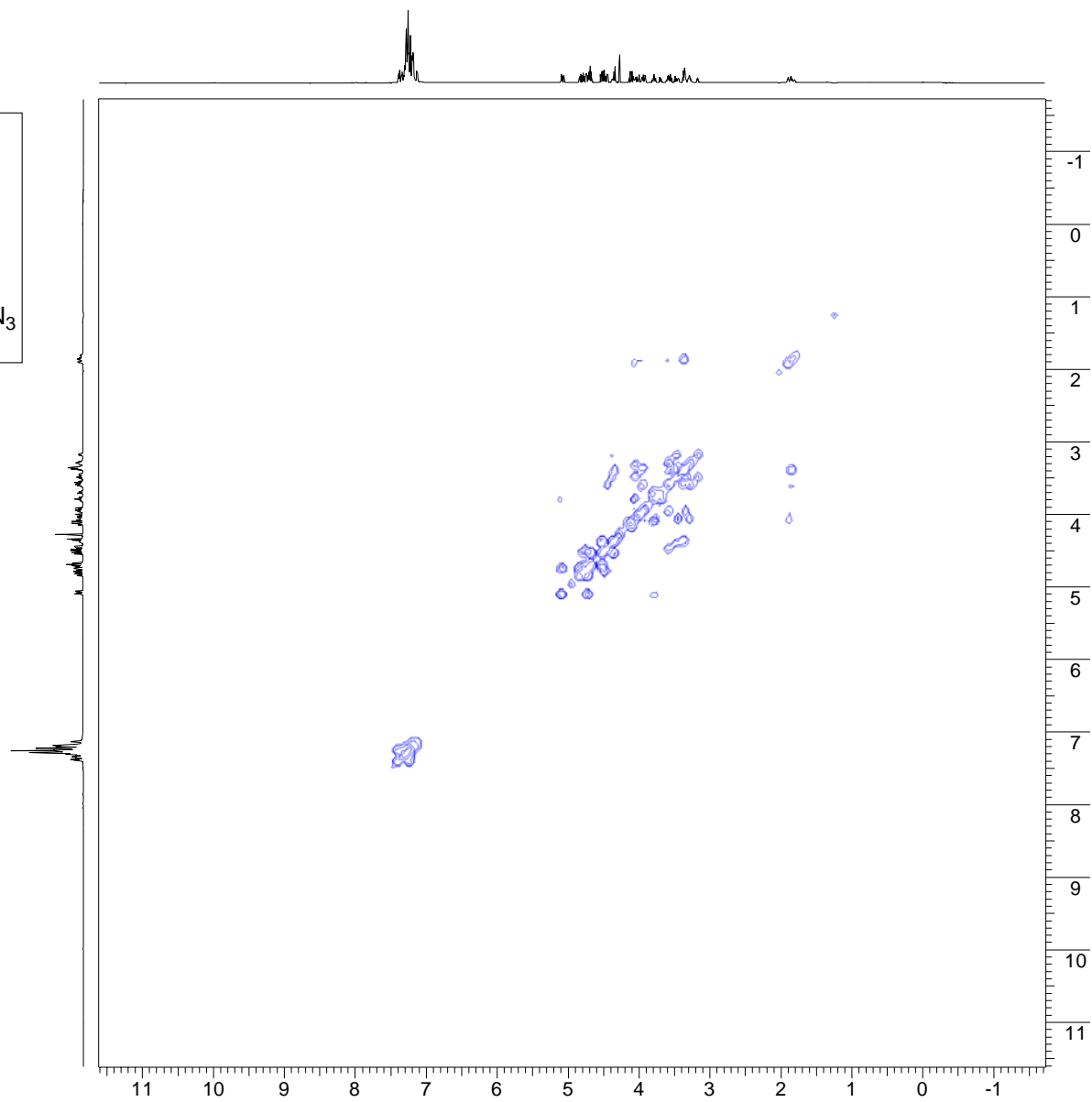
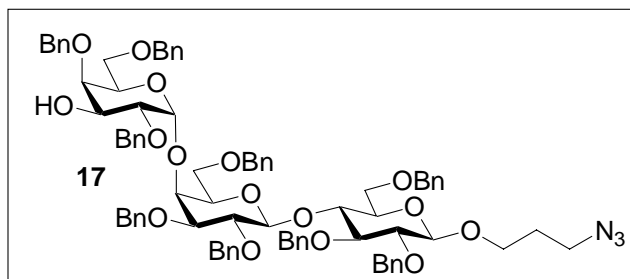
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C-NMR}$  (150 MHz,  $\text{CDCl}_3$ )

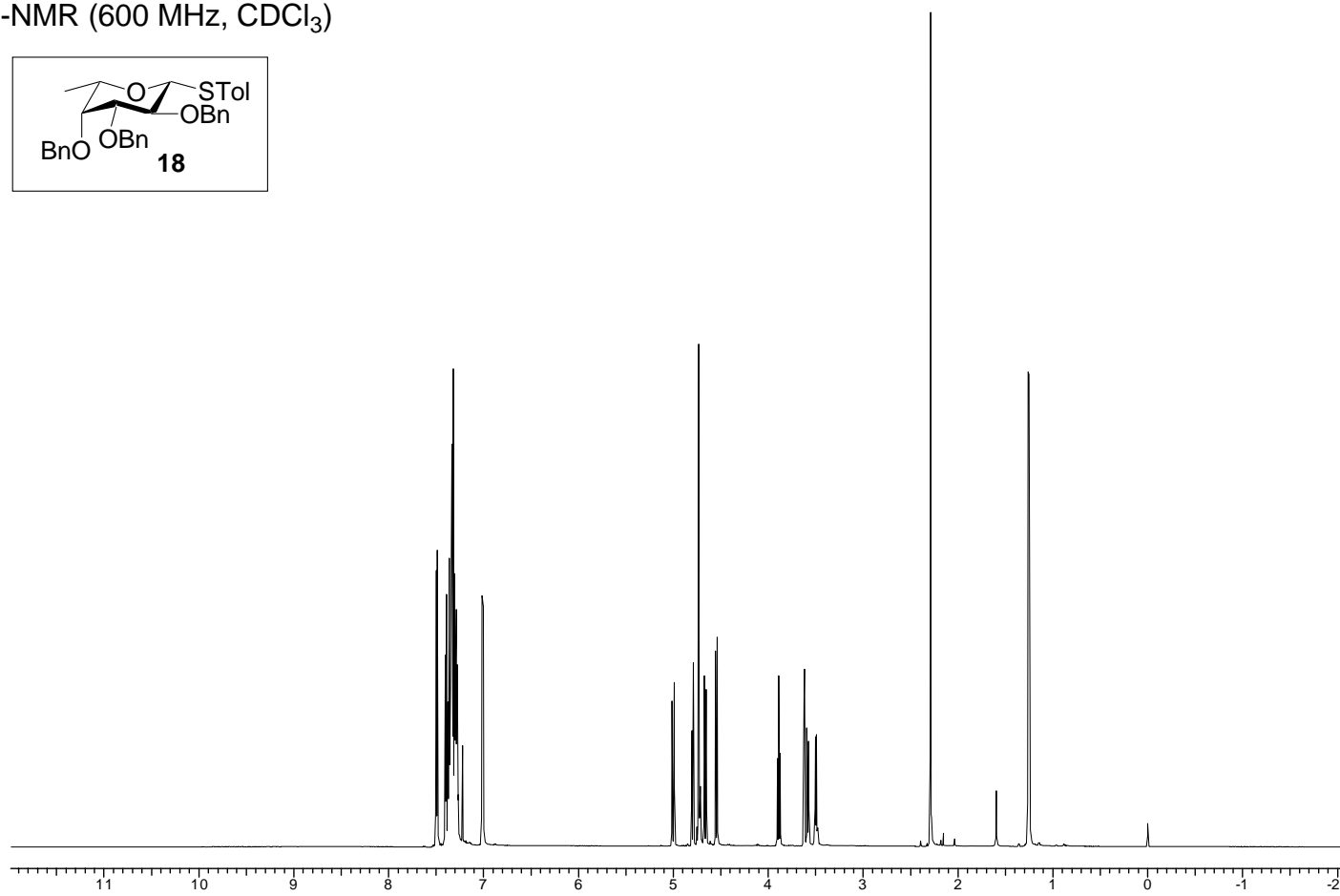
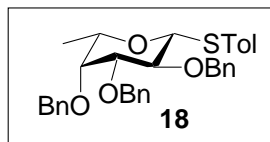


gCOSY (600 MHz, CDCl<sub>3</sub>)

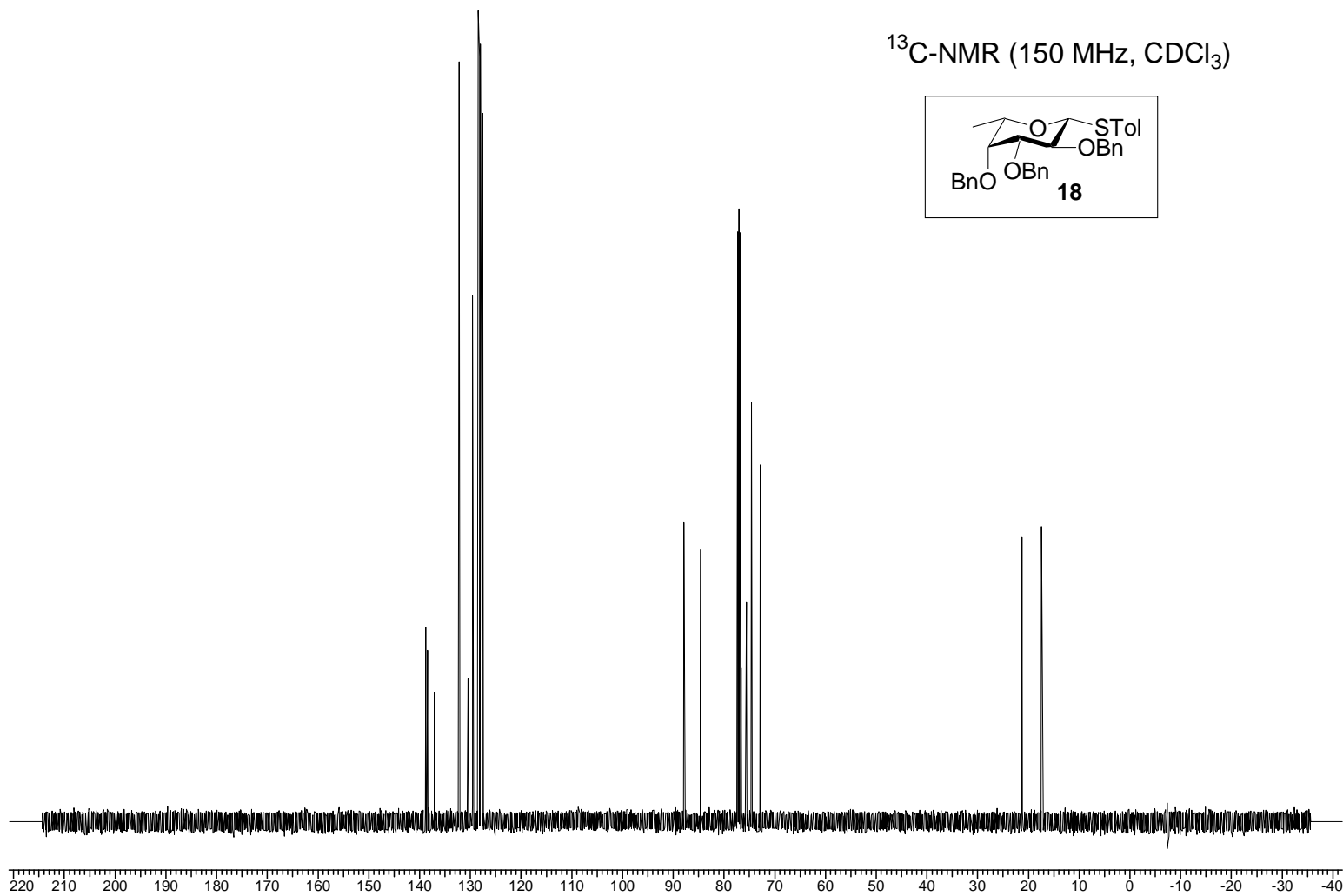
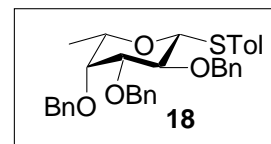




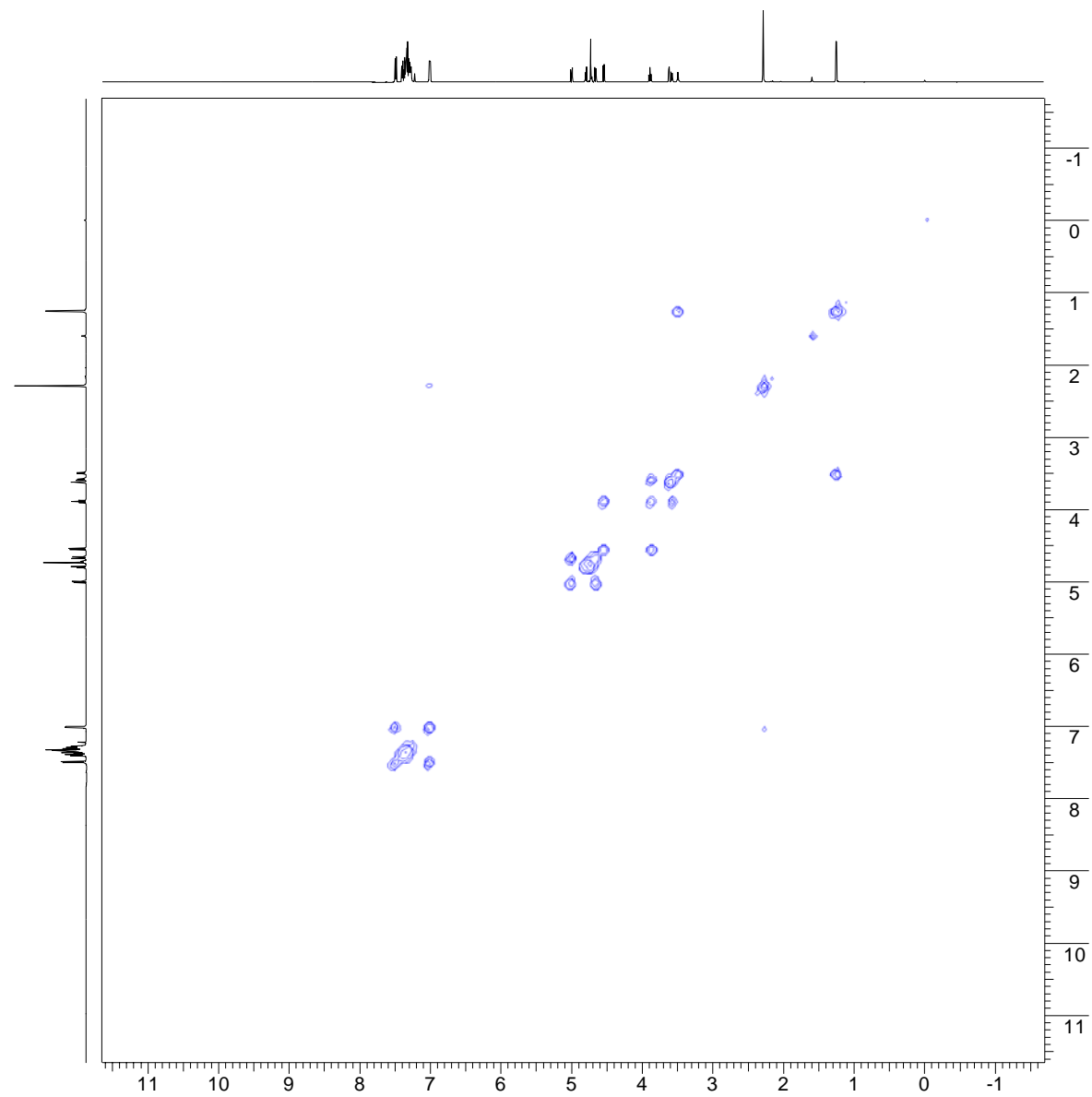
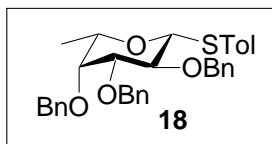
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



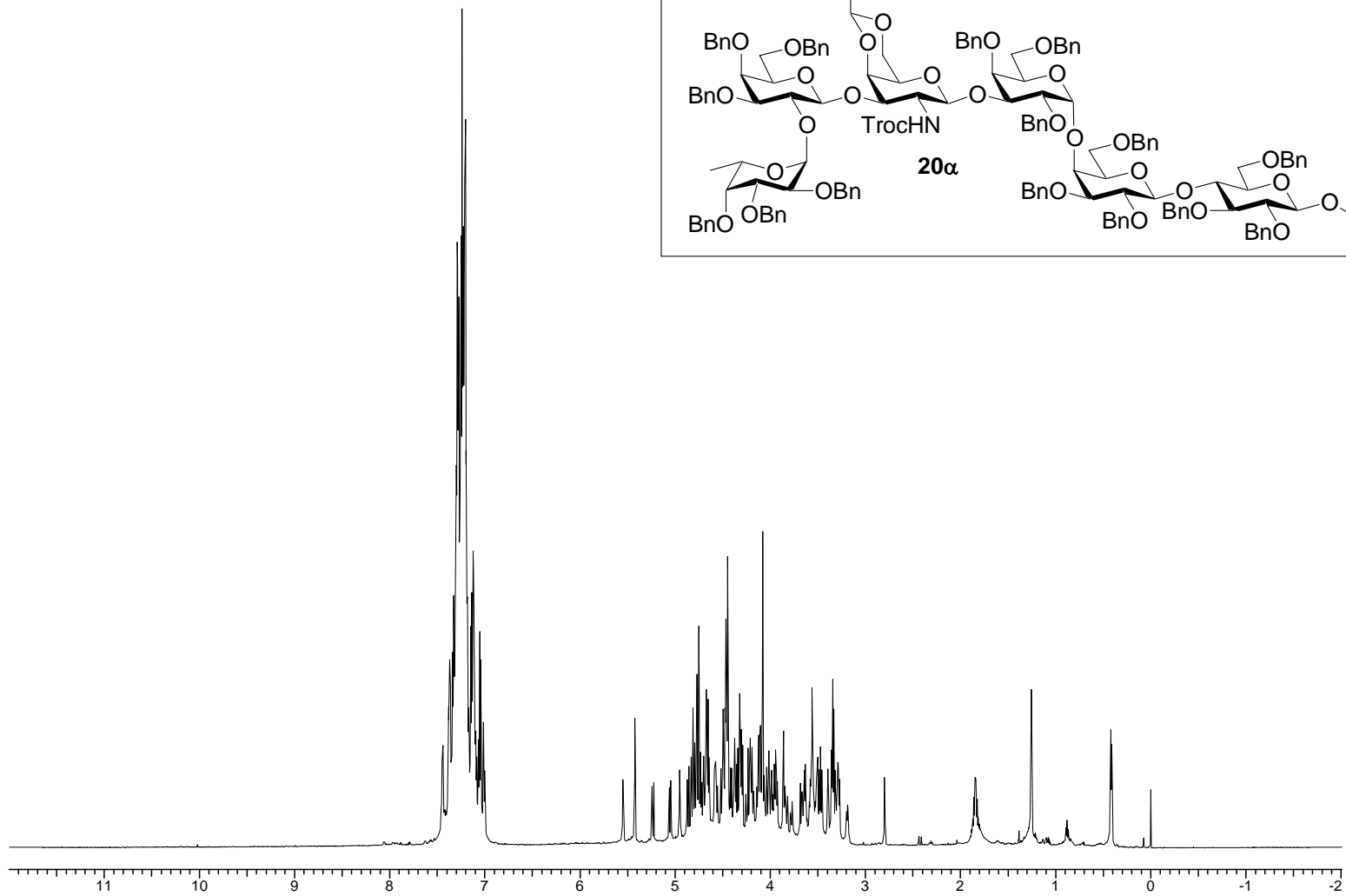
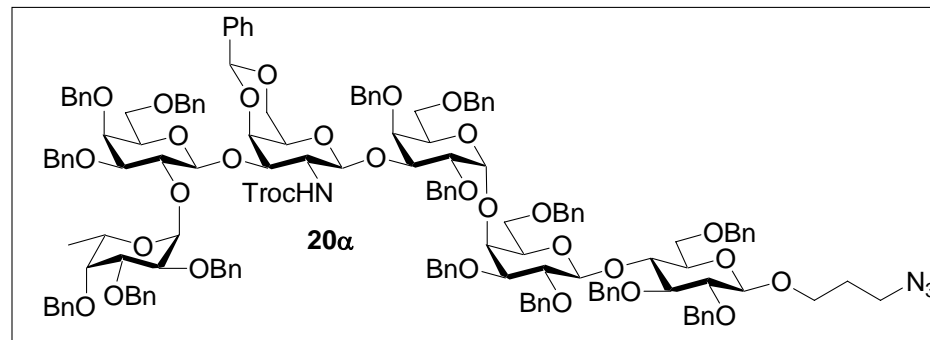
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



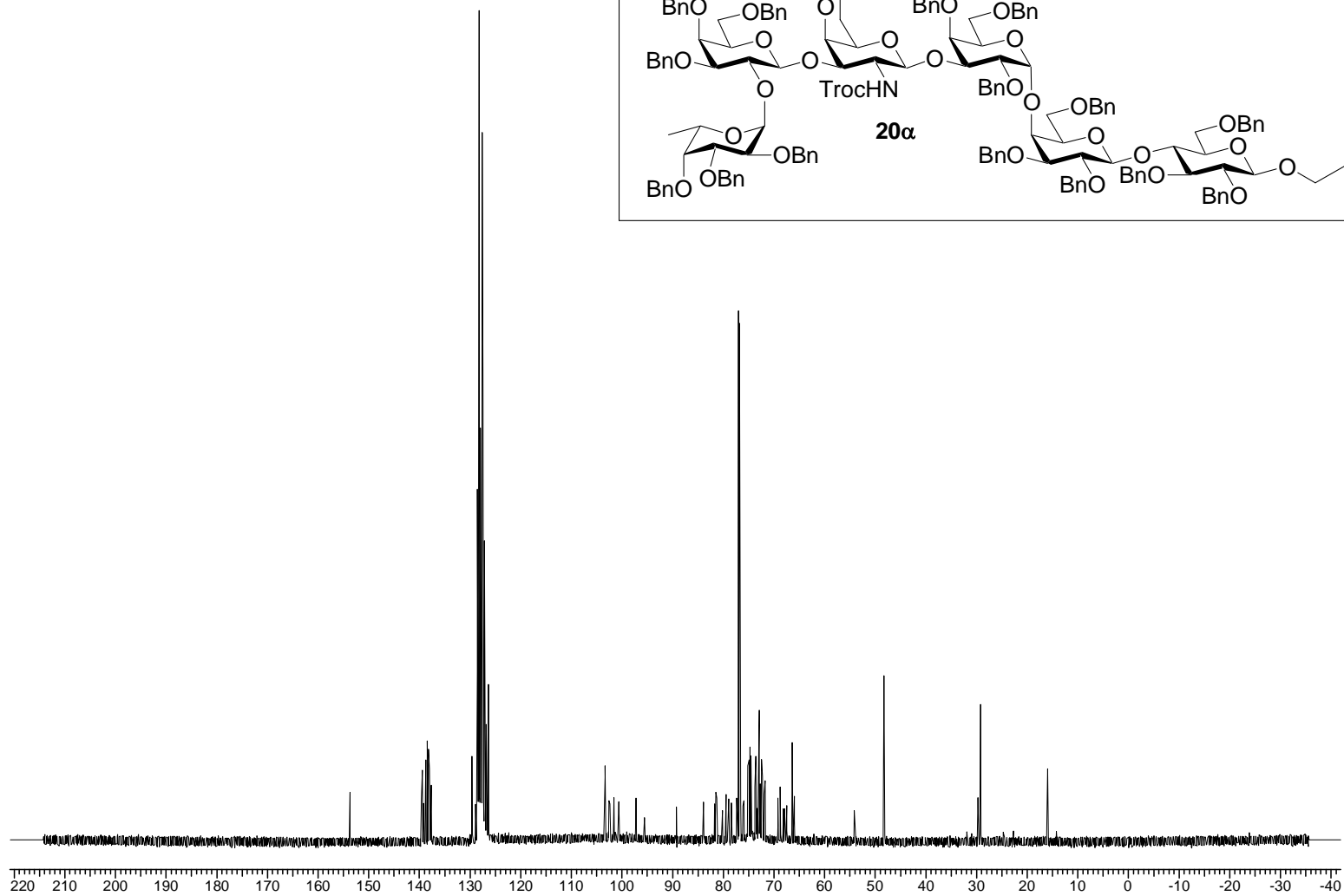
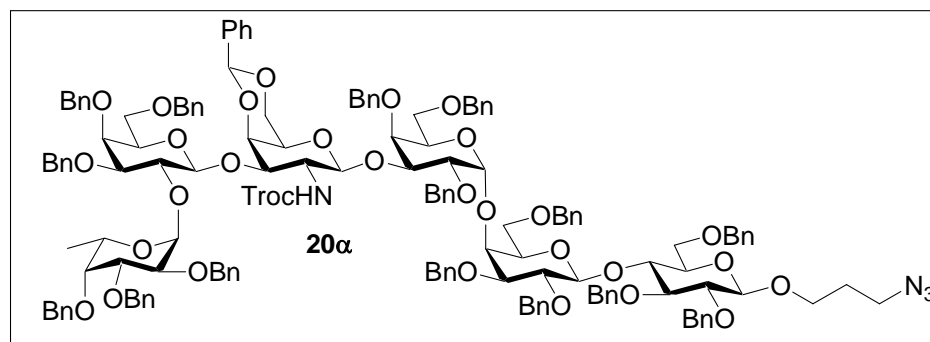
gCOSY (600 MHz, CDCl<sub>3</sub>)



$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

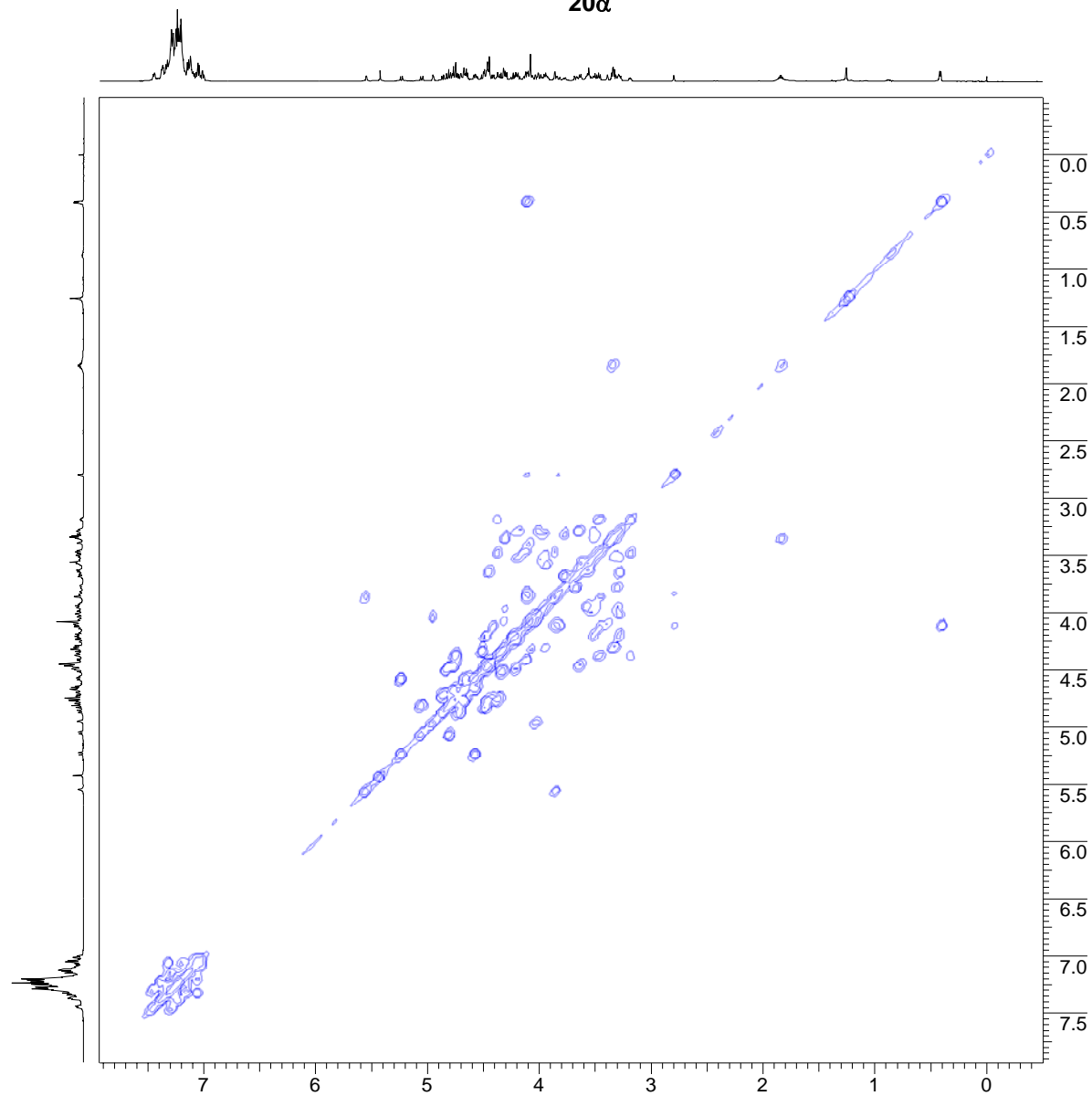


$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



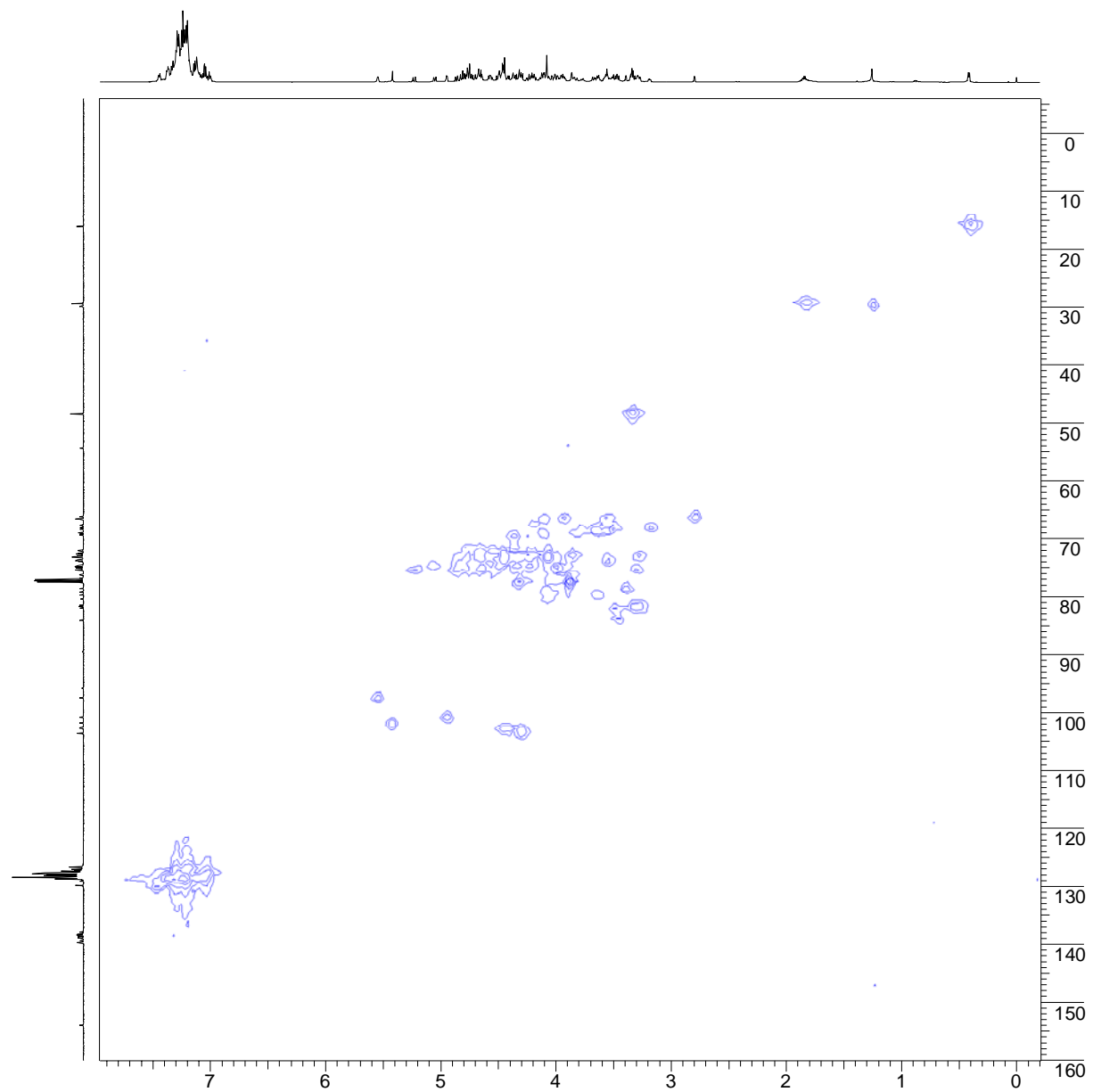
gCOSY (600 MHz, CDCl<sub>3</sub>)

20α

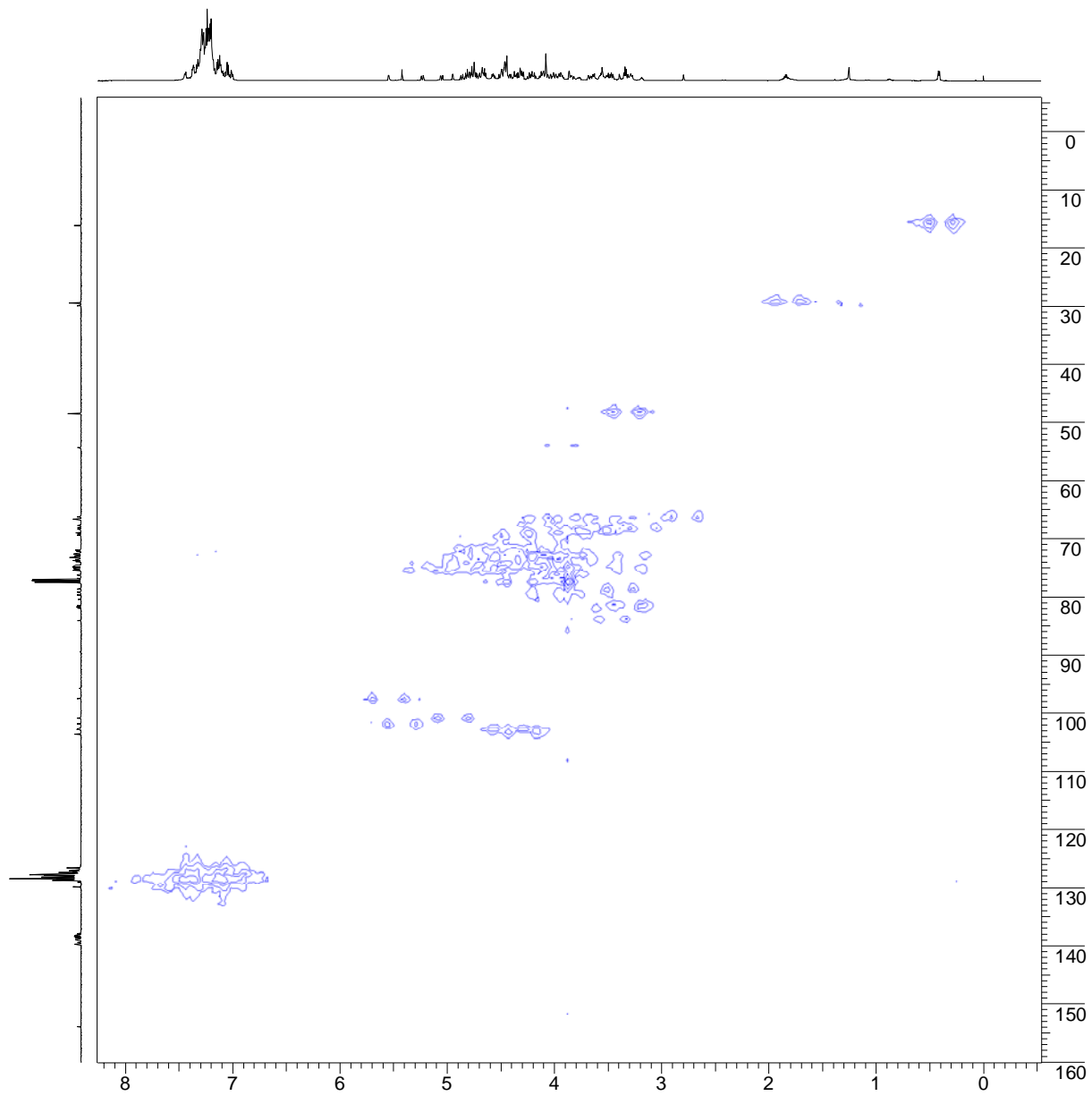


gHMQC (600 MHz, CDCl<sub>3</sub>)

20α

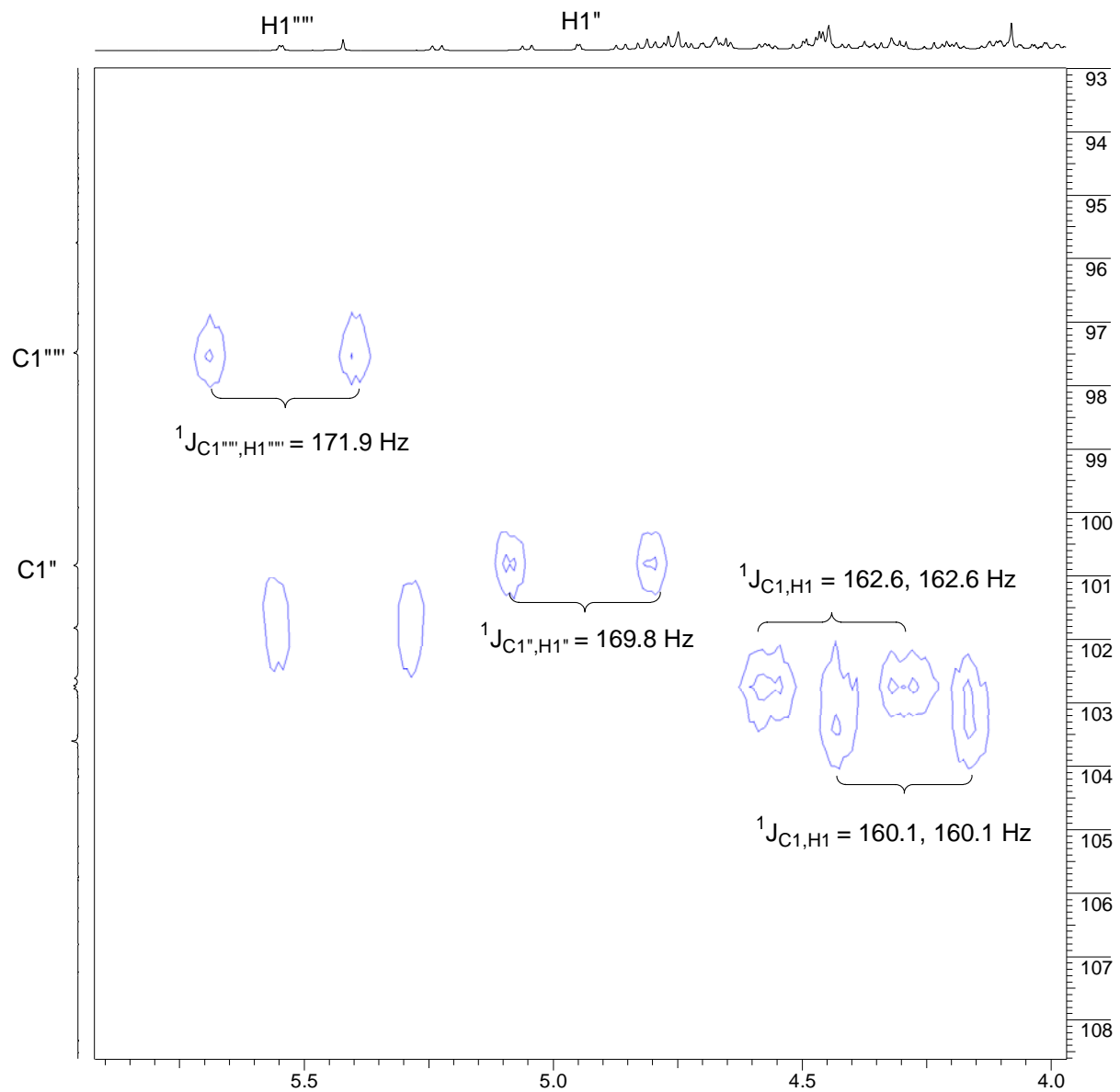


gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )  
**20 $\alpha$**

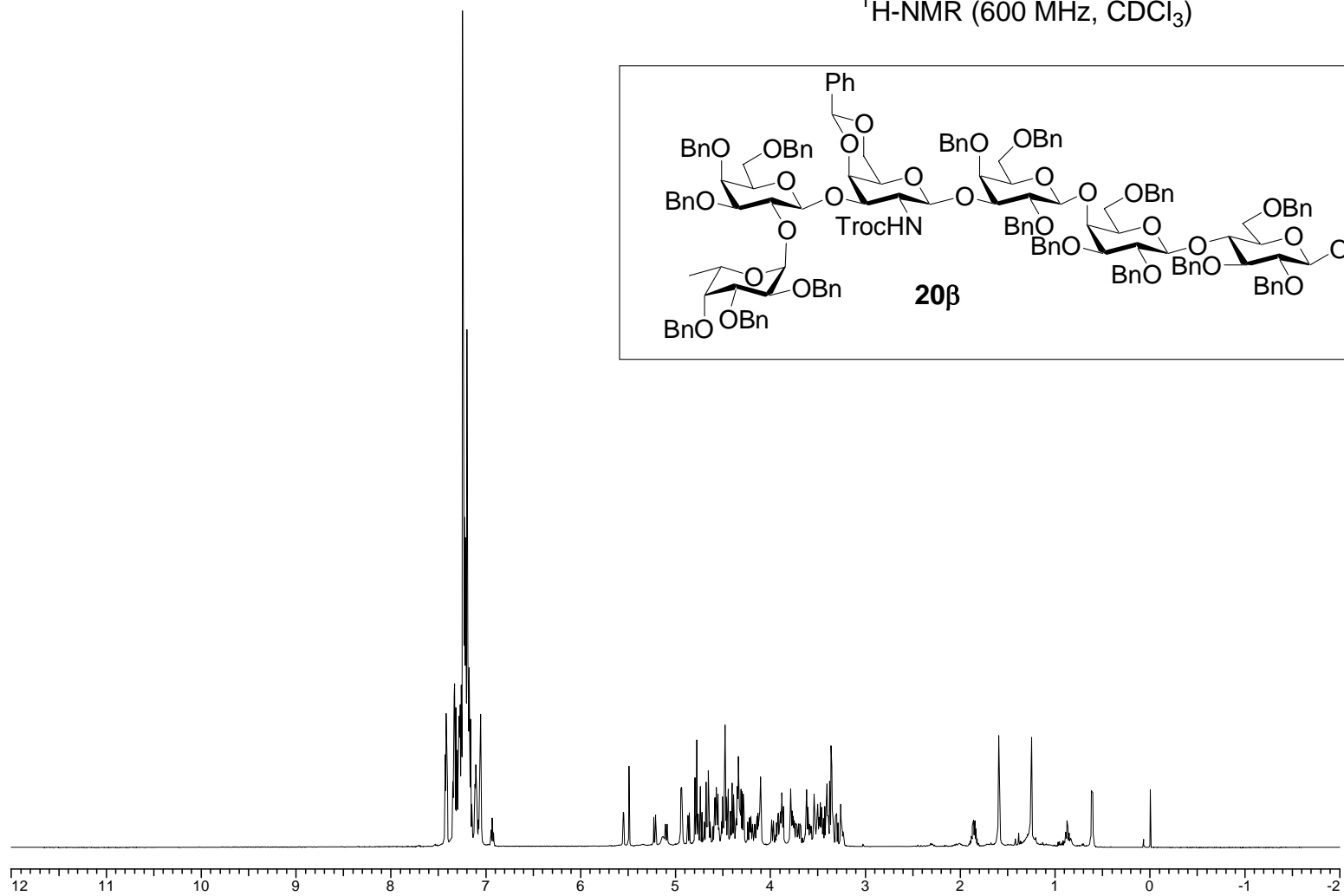
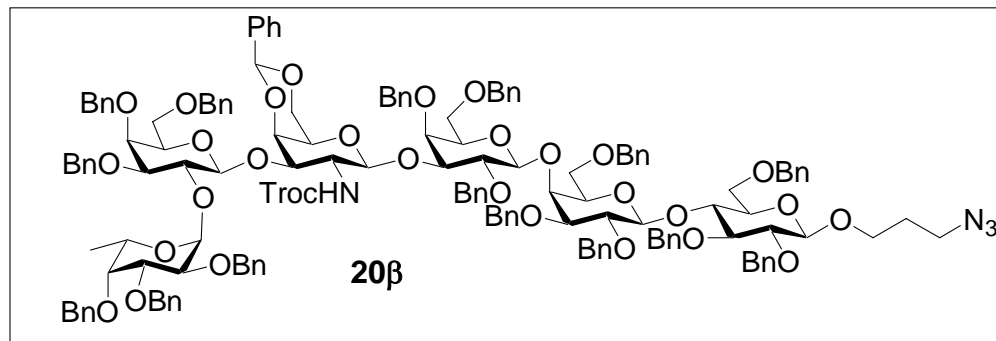




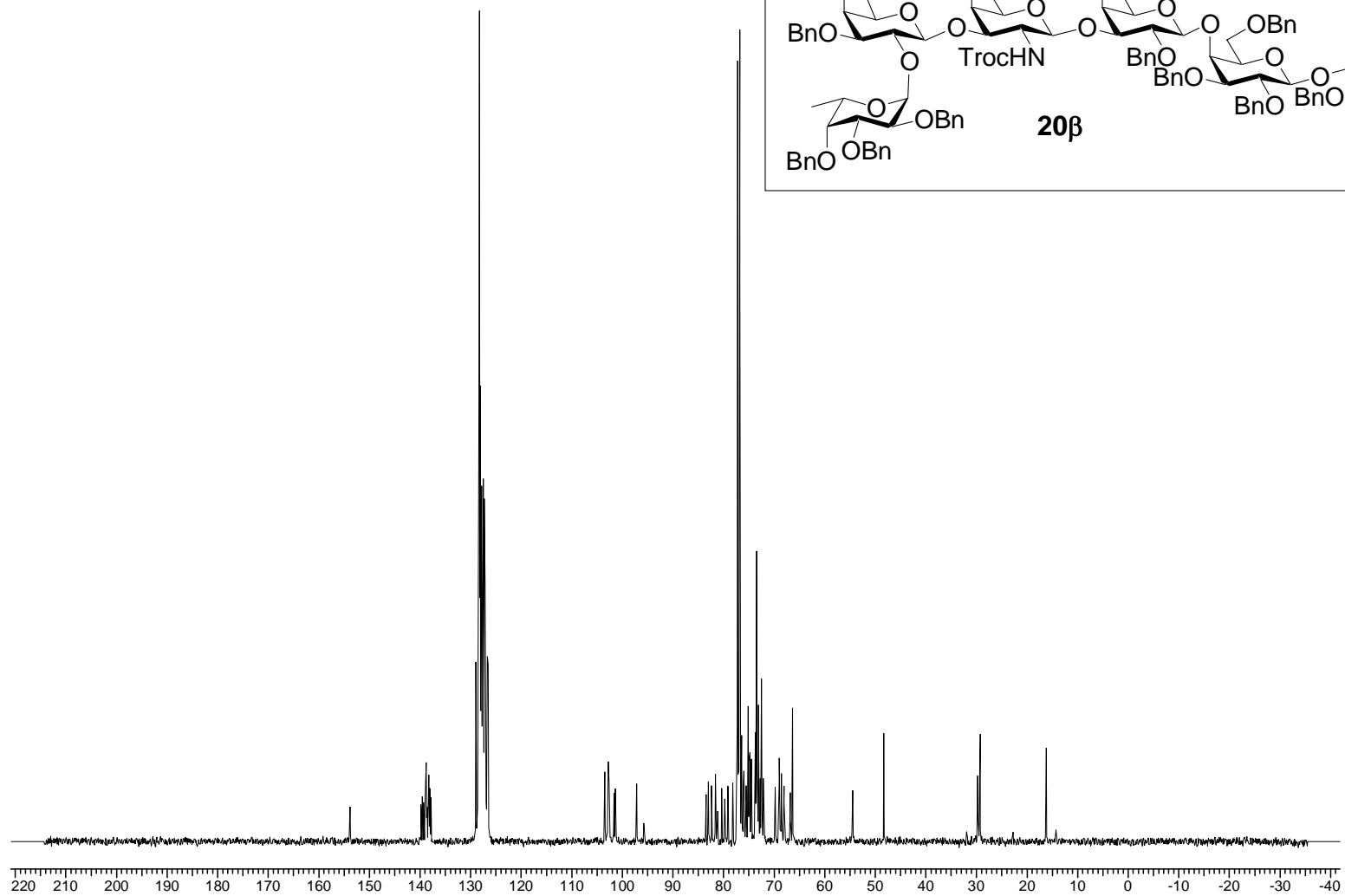
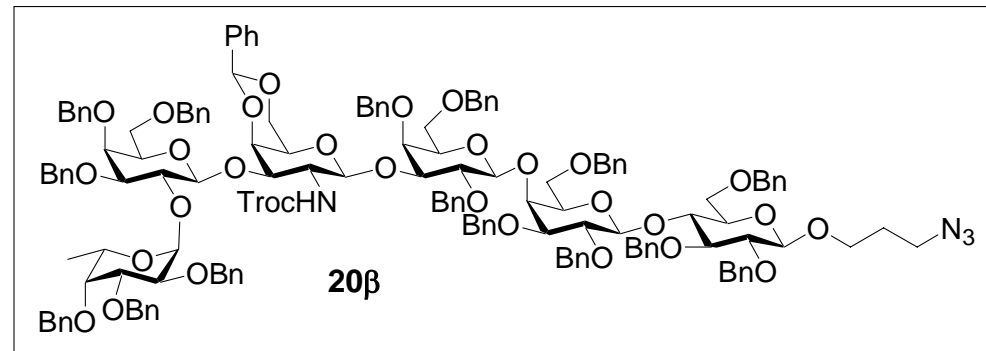
gHMQC (without 1H decoupling)  
(600 MHz, CDCl<sub>3</sub>)  
**20α**



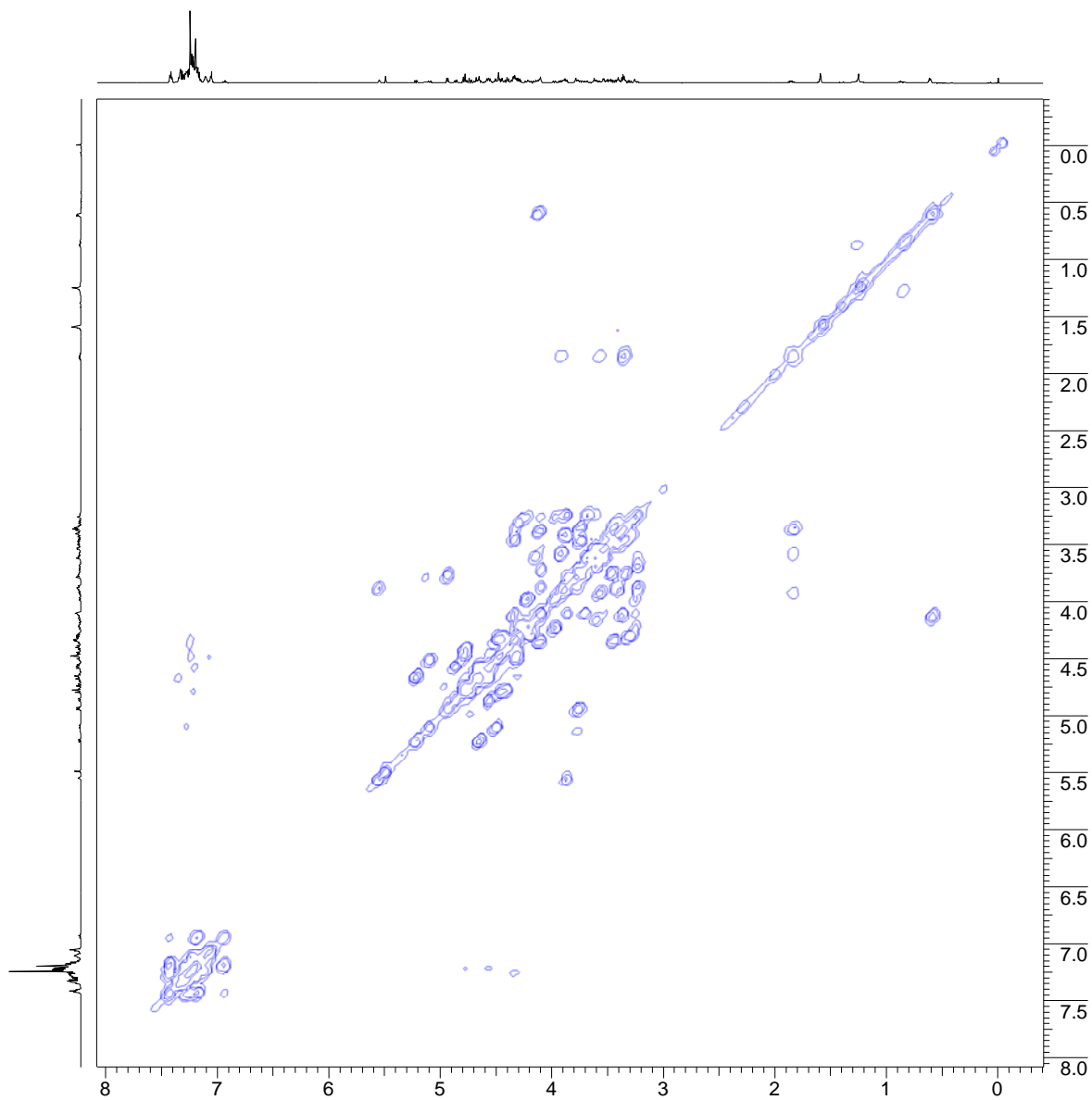
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )

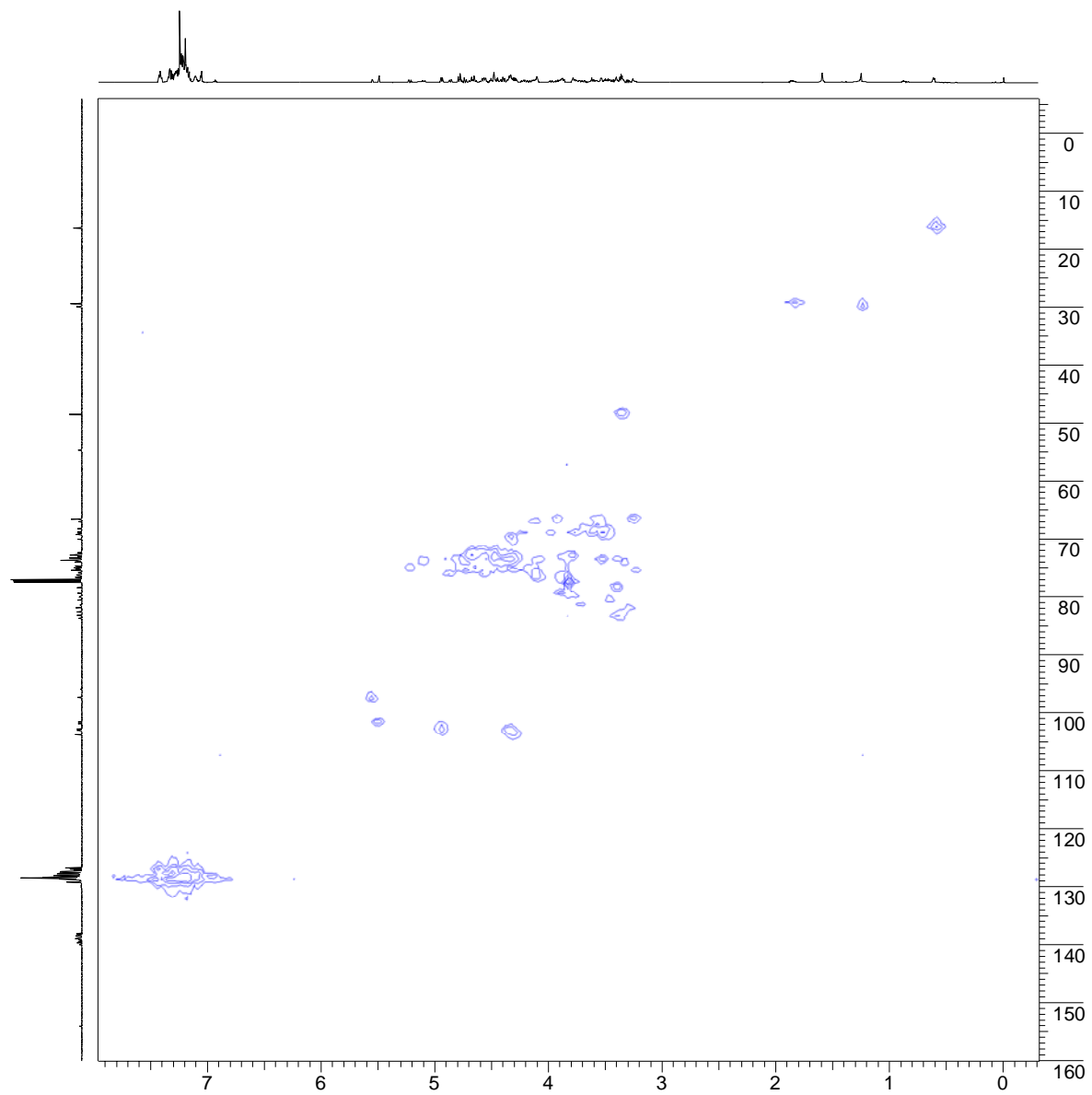


gCOSY (600 MHz, CDCl<sub>3</sub>)  
20β



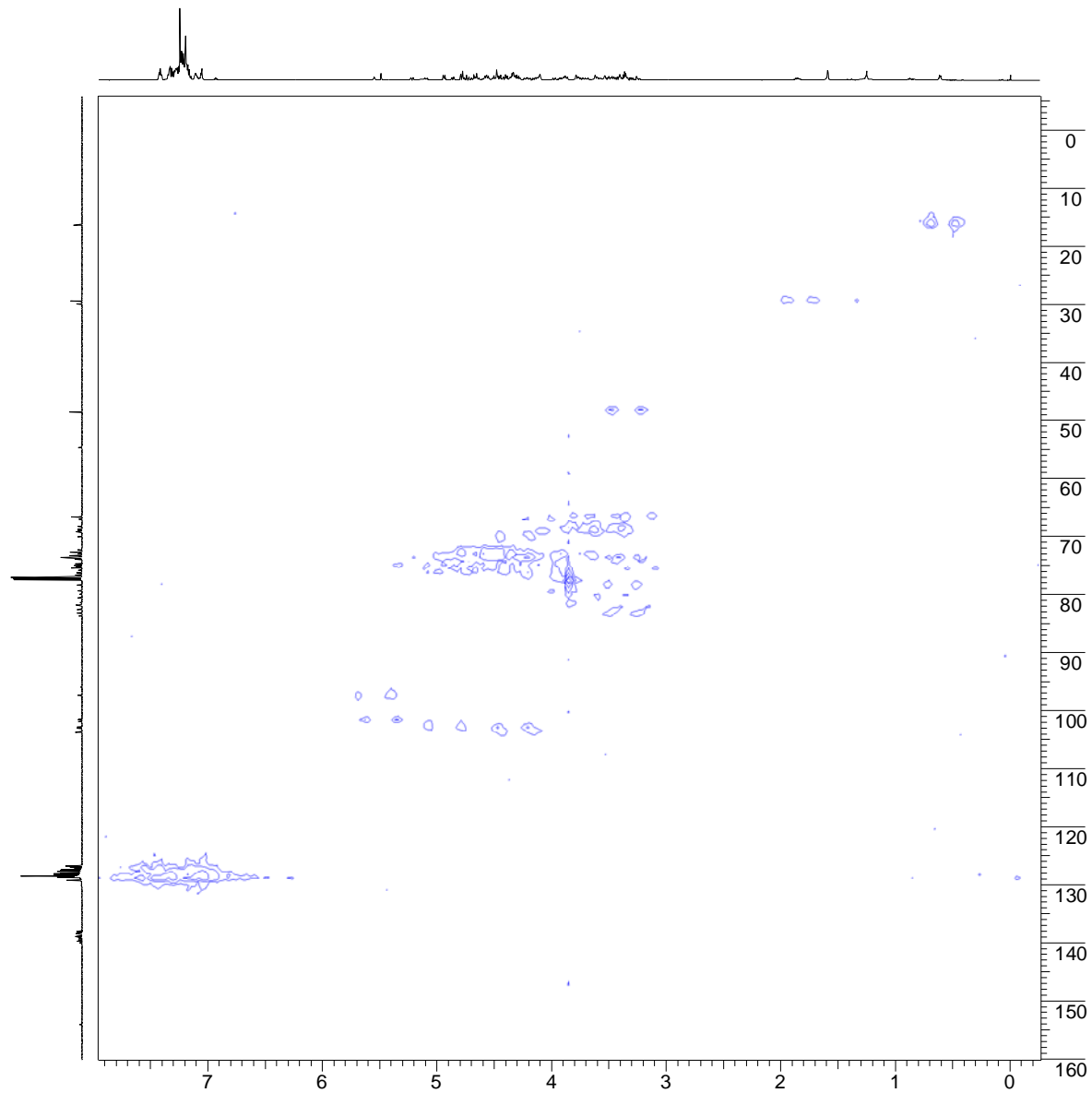
gHMQC (600 MHz, CDCl<sub>3</sub>)

20β

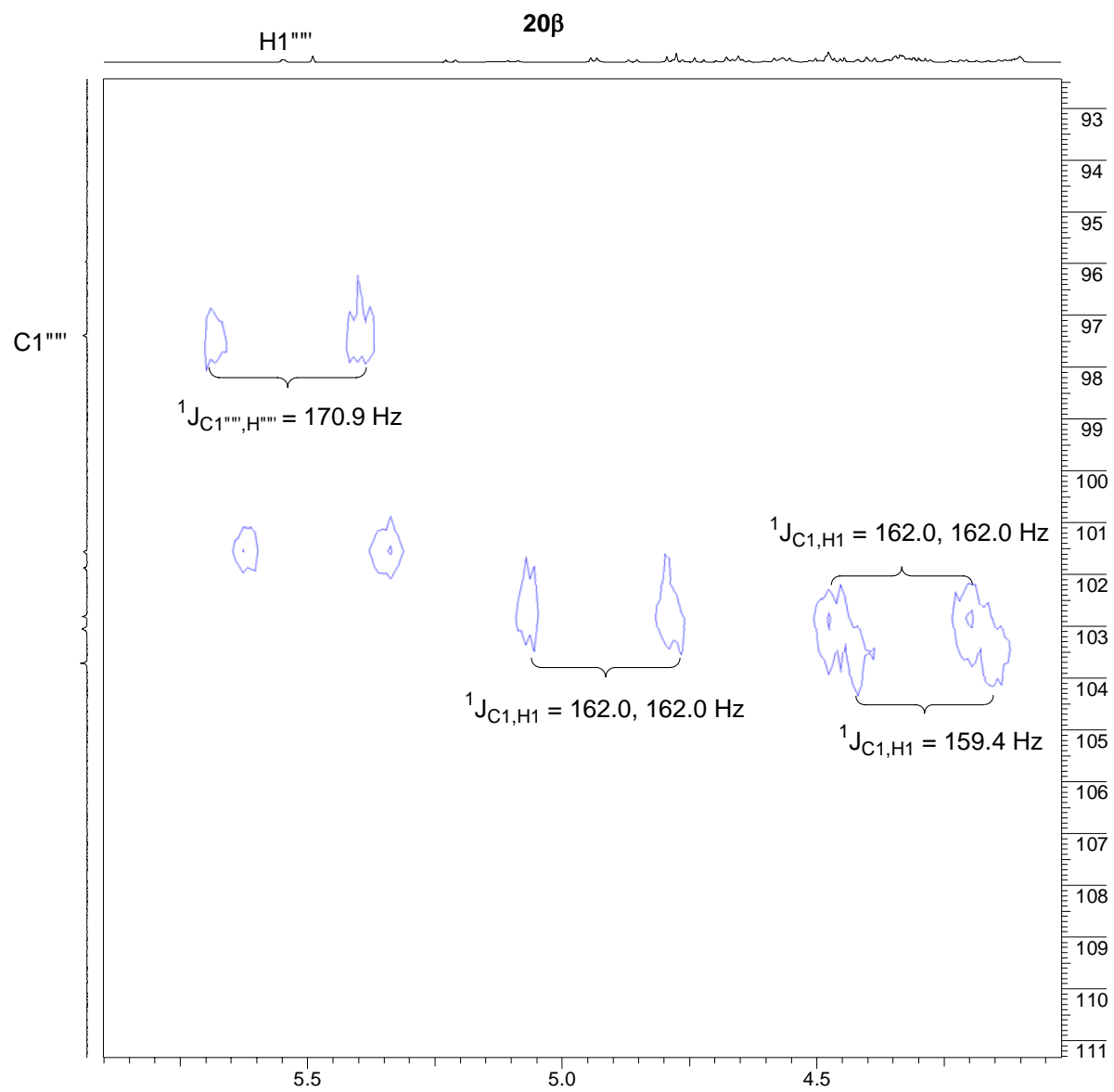


gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )

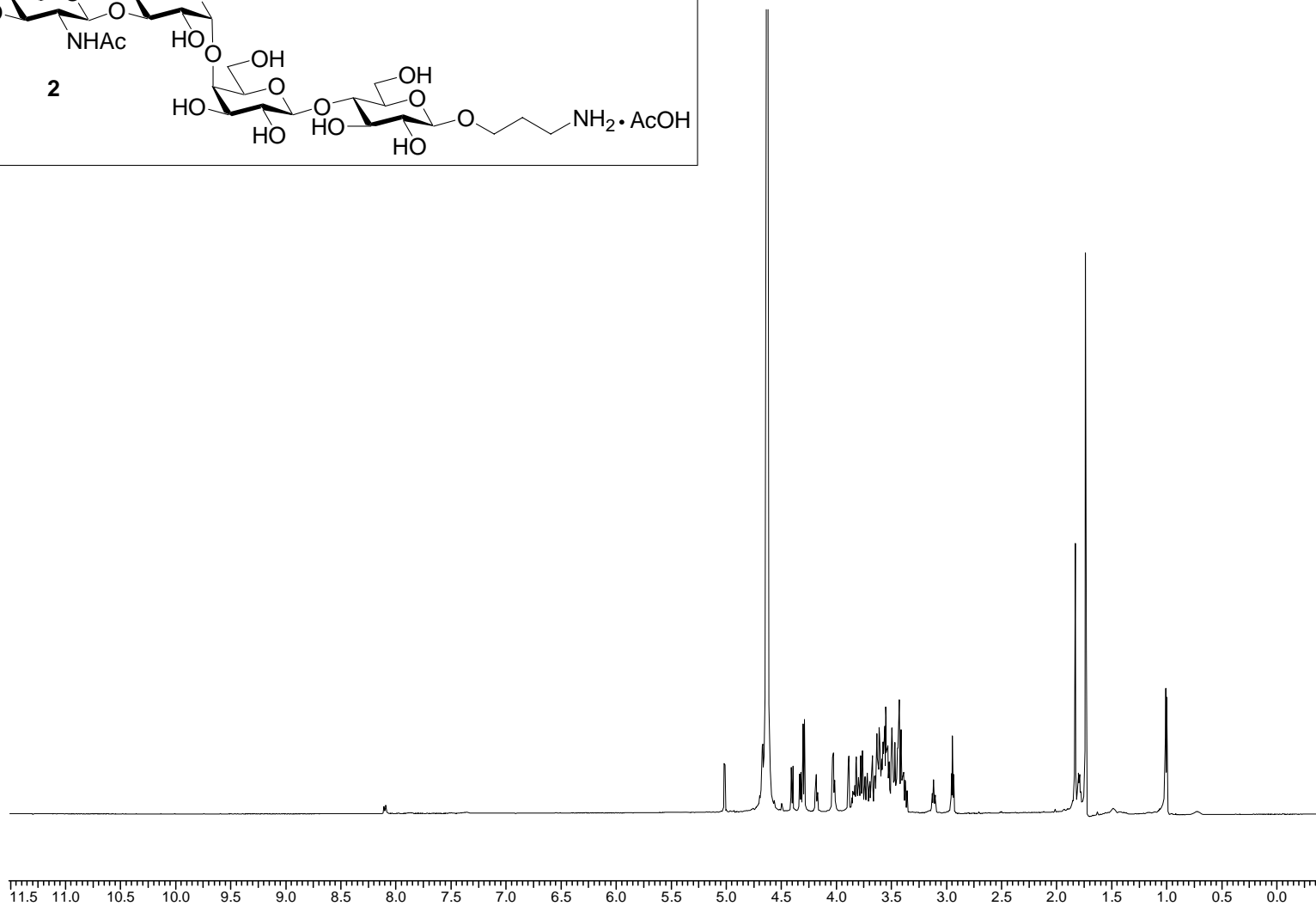
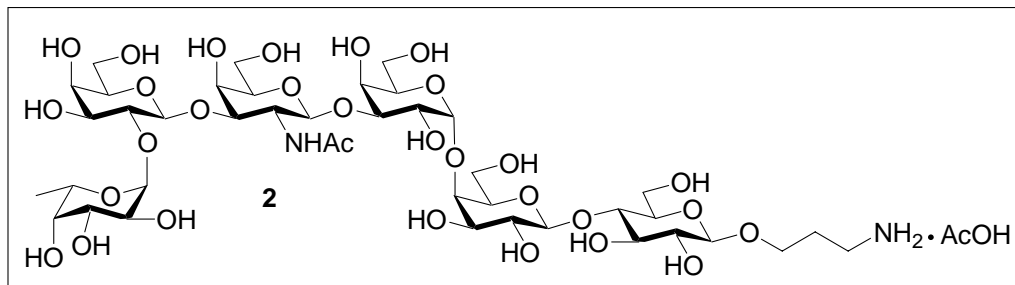
$20\beta$



gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{CDCl}_3$ )

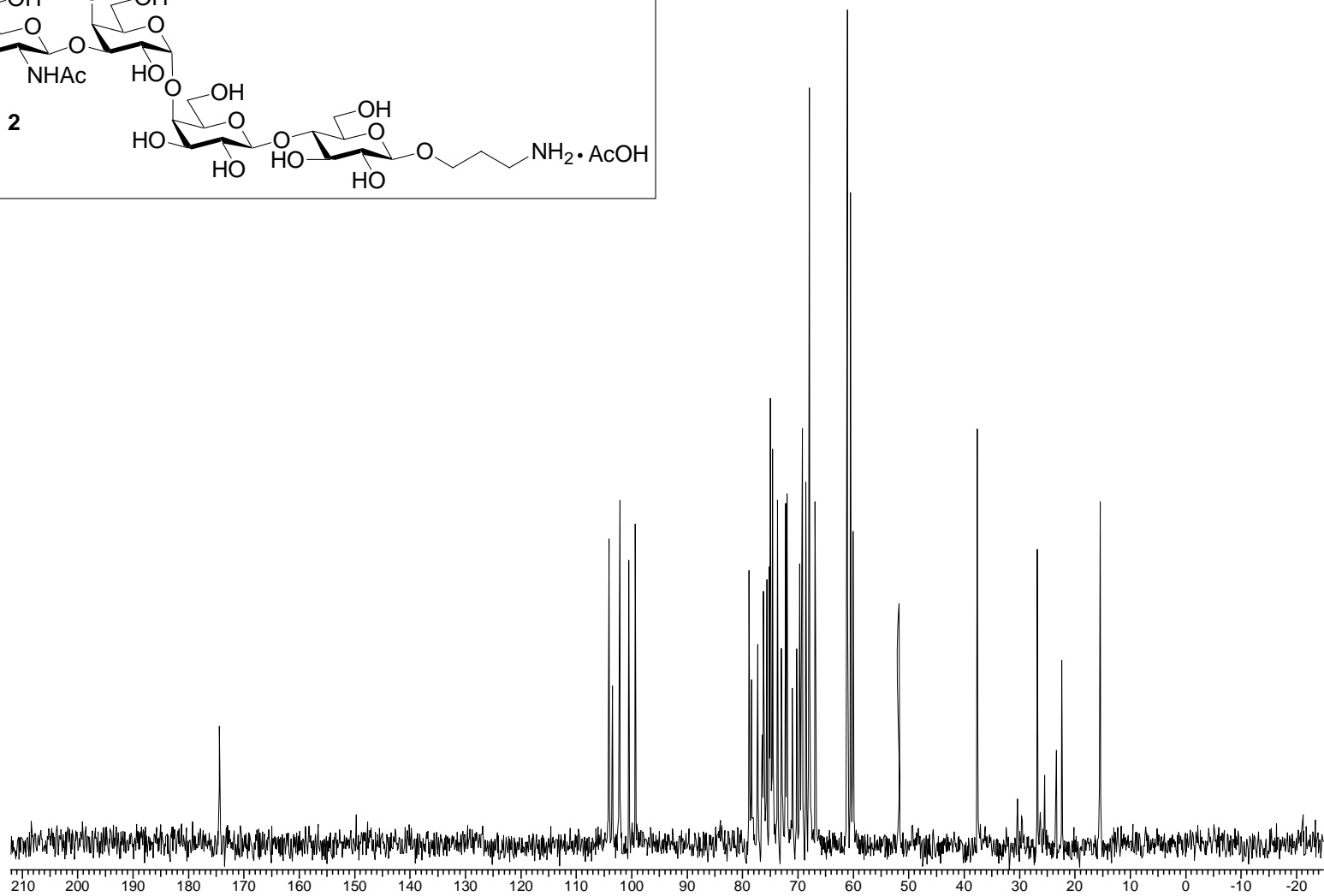
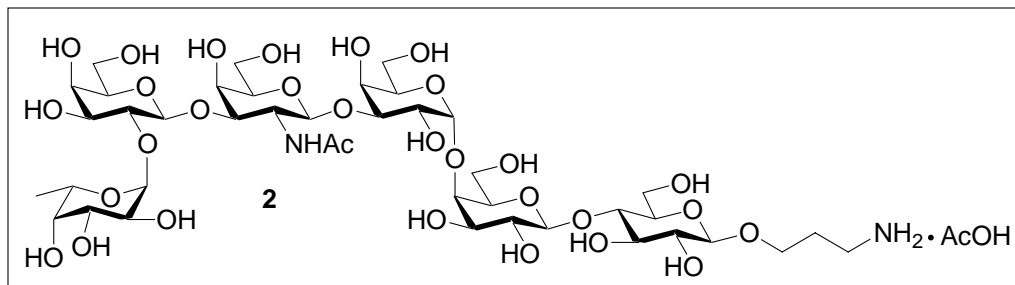


$^1\text{H-NMR}$  (600 MHz,  $\text{D}_2\text{O}$ )



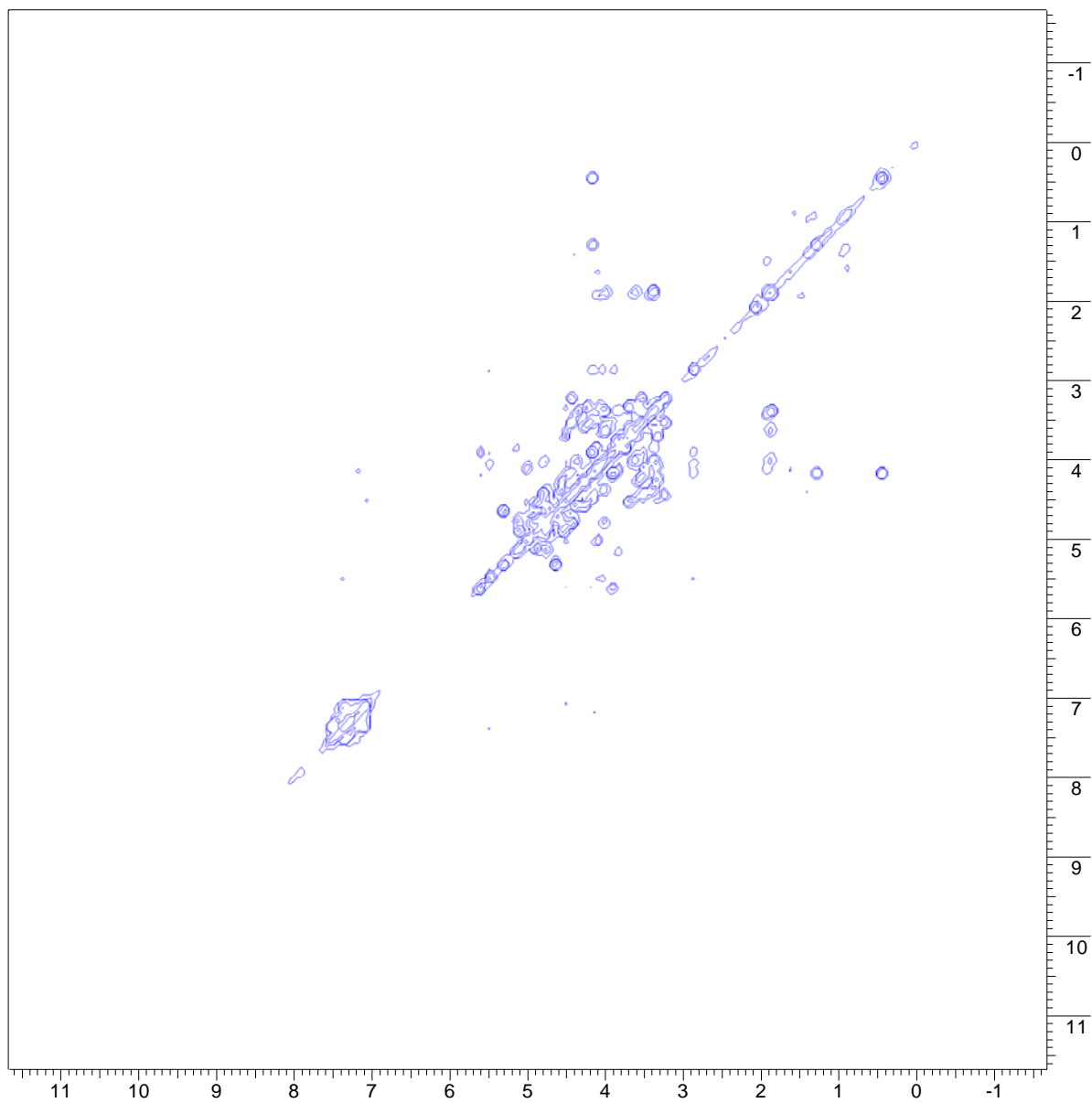


$^{13}\text{C}$ -NMR (150 MHz,  $\text{D}_2\text{O}$ )



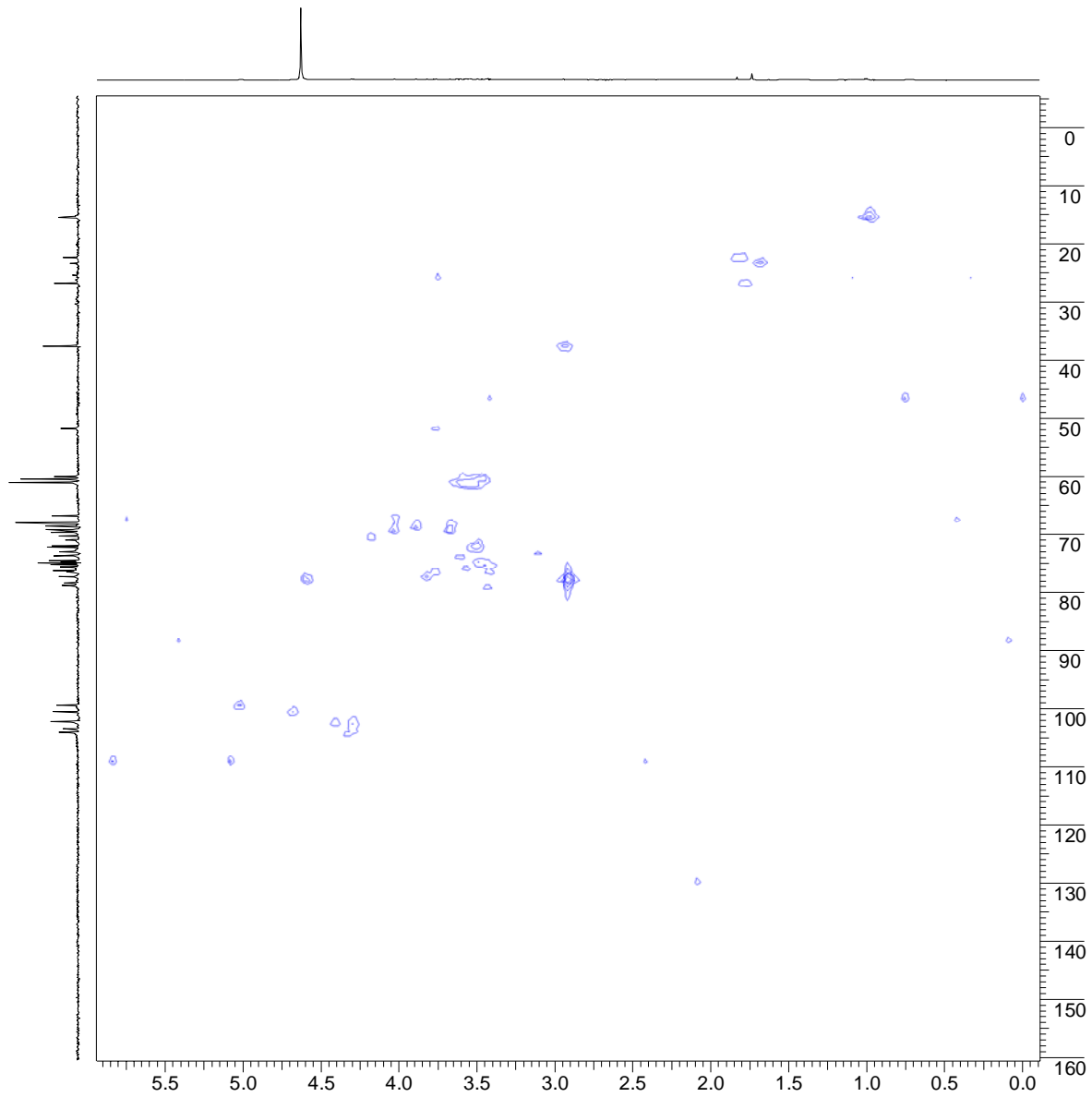
gCOSY (600 MHz, D<sub>2</sub>O)

2



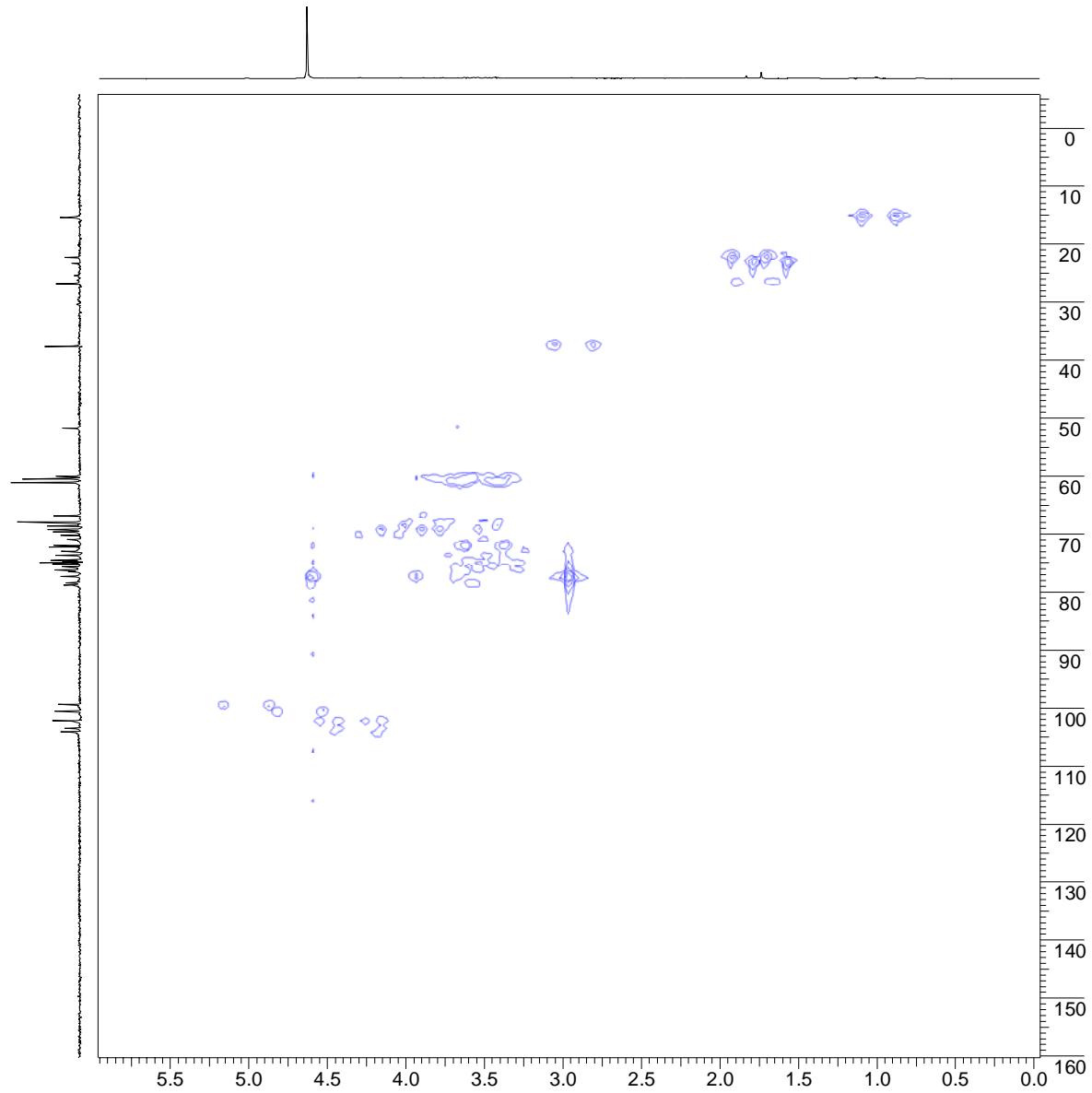
gHMQC (600 MHz, D<sub>2</sub>O)

2



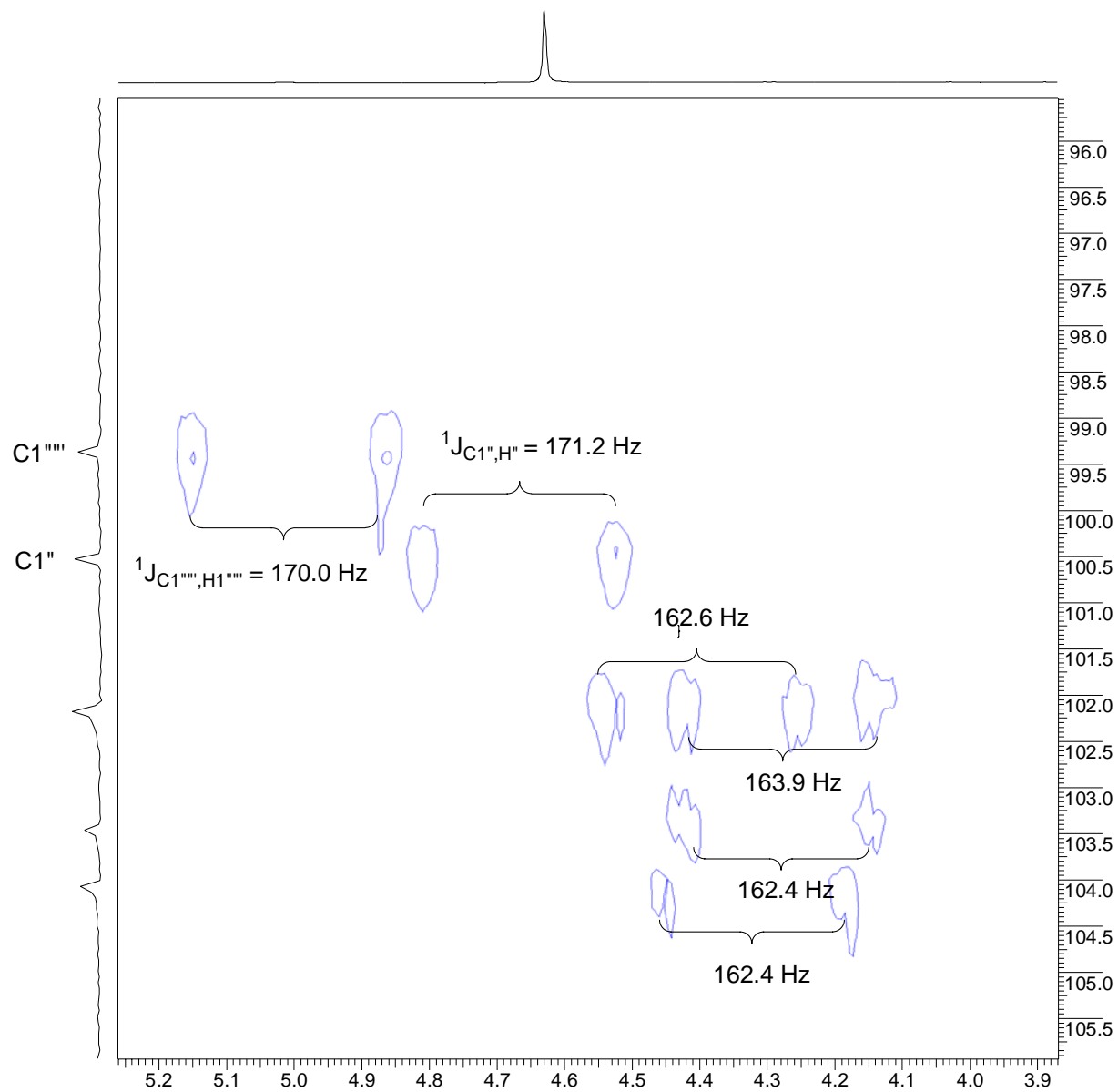
gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{D}_2\text{O}$ )

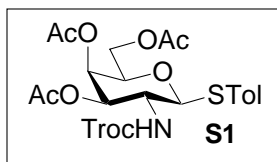
2



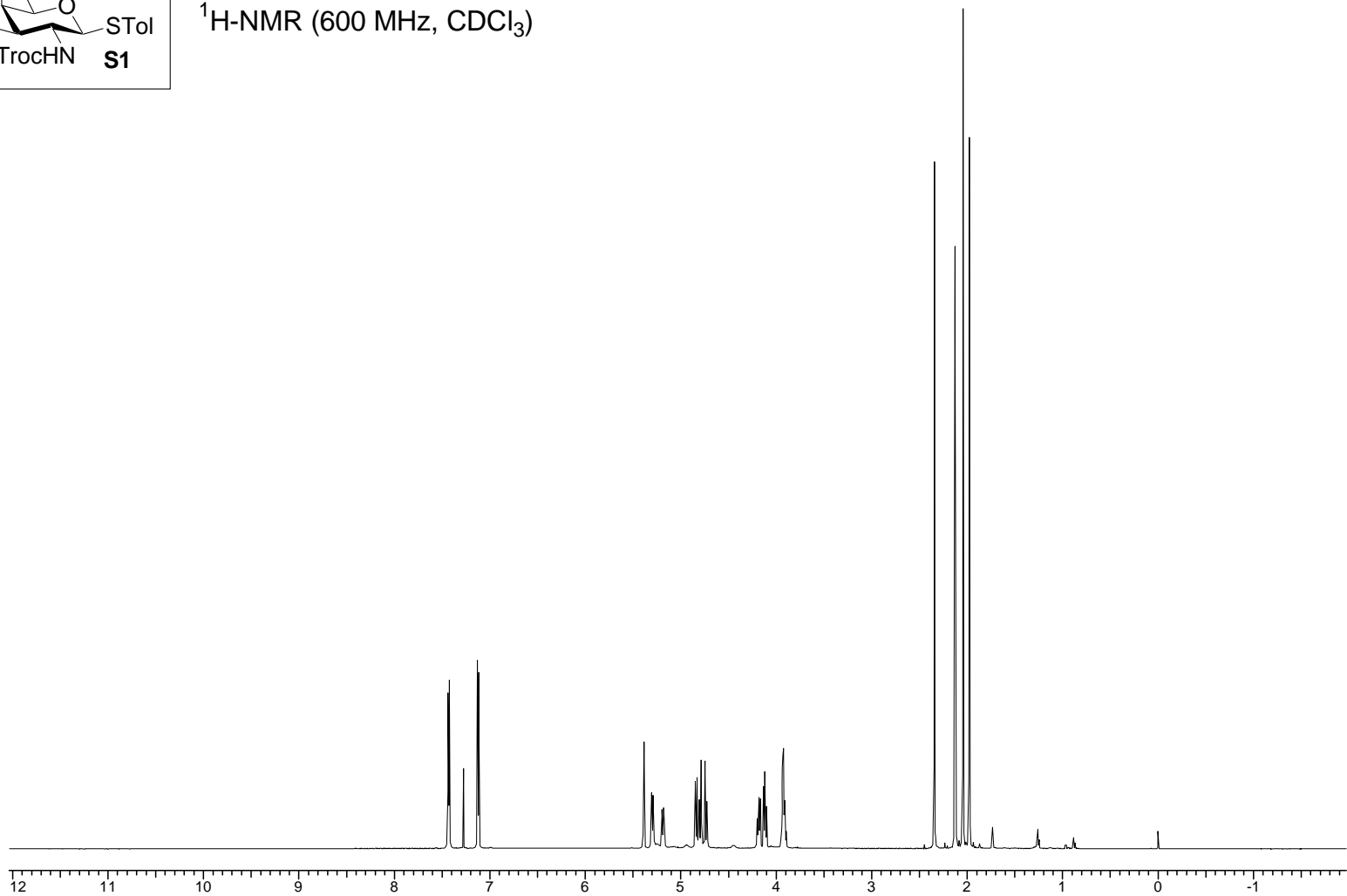
gHMQC (without  $^1\text{H}$  decoupling)  
(600 MHz,  $\text{D}_2\text{O}$ )

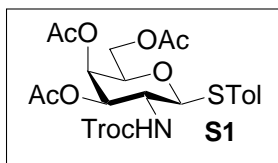
2



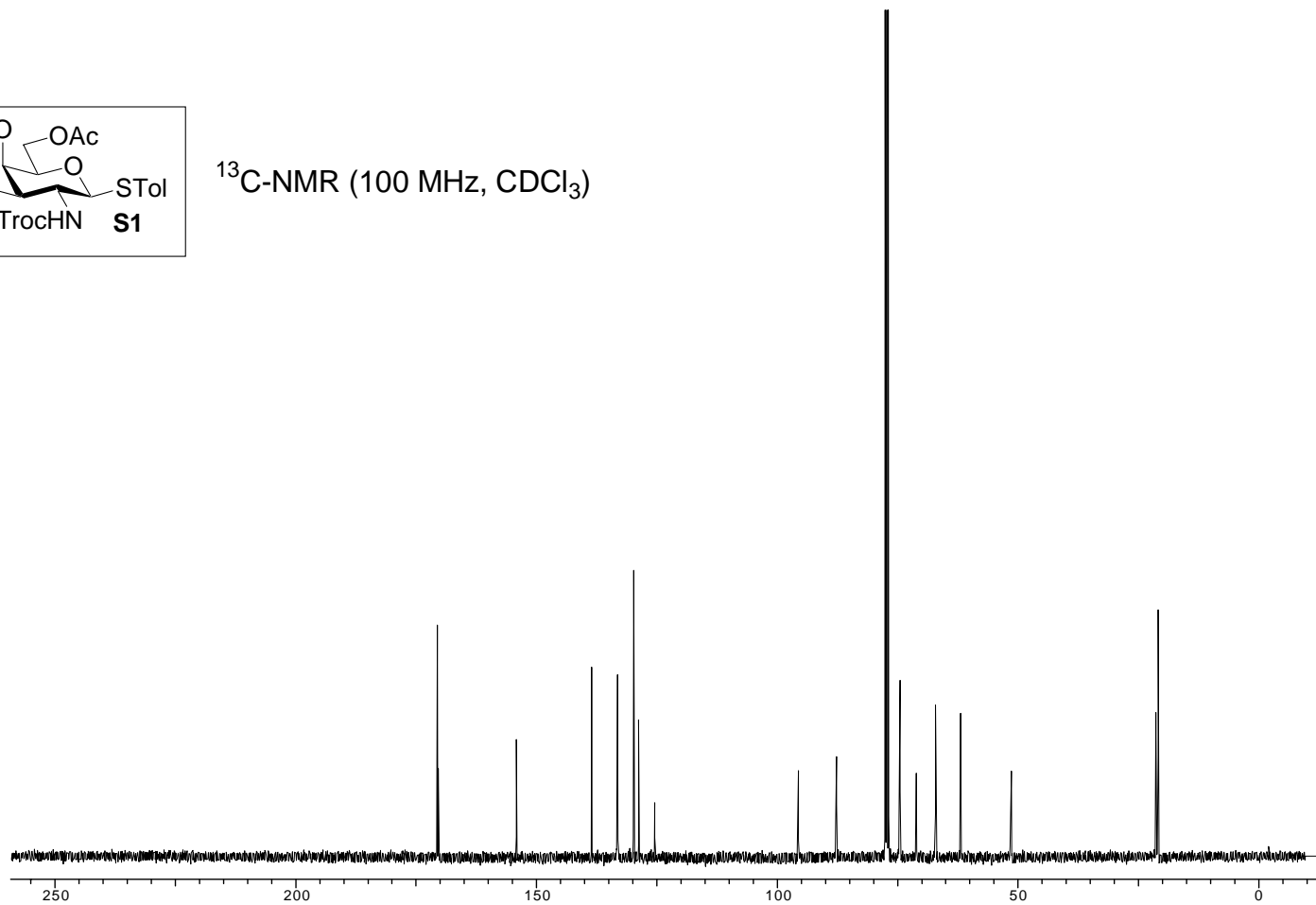


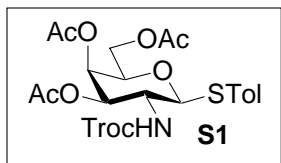
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



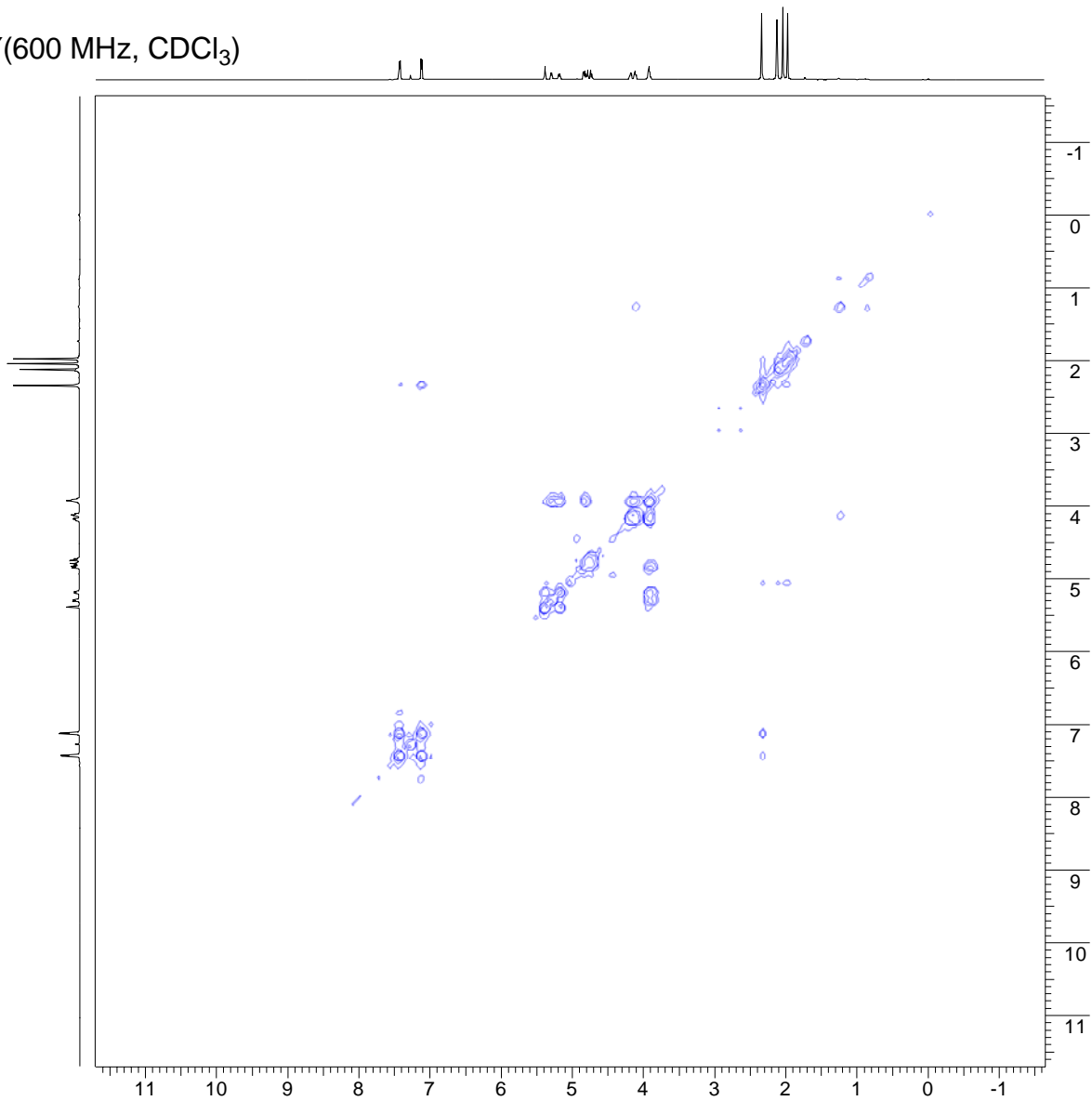


$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )

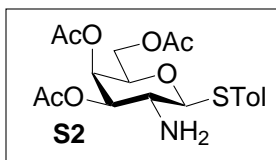




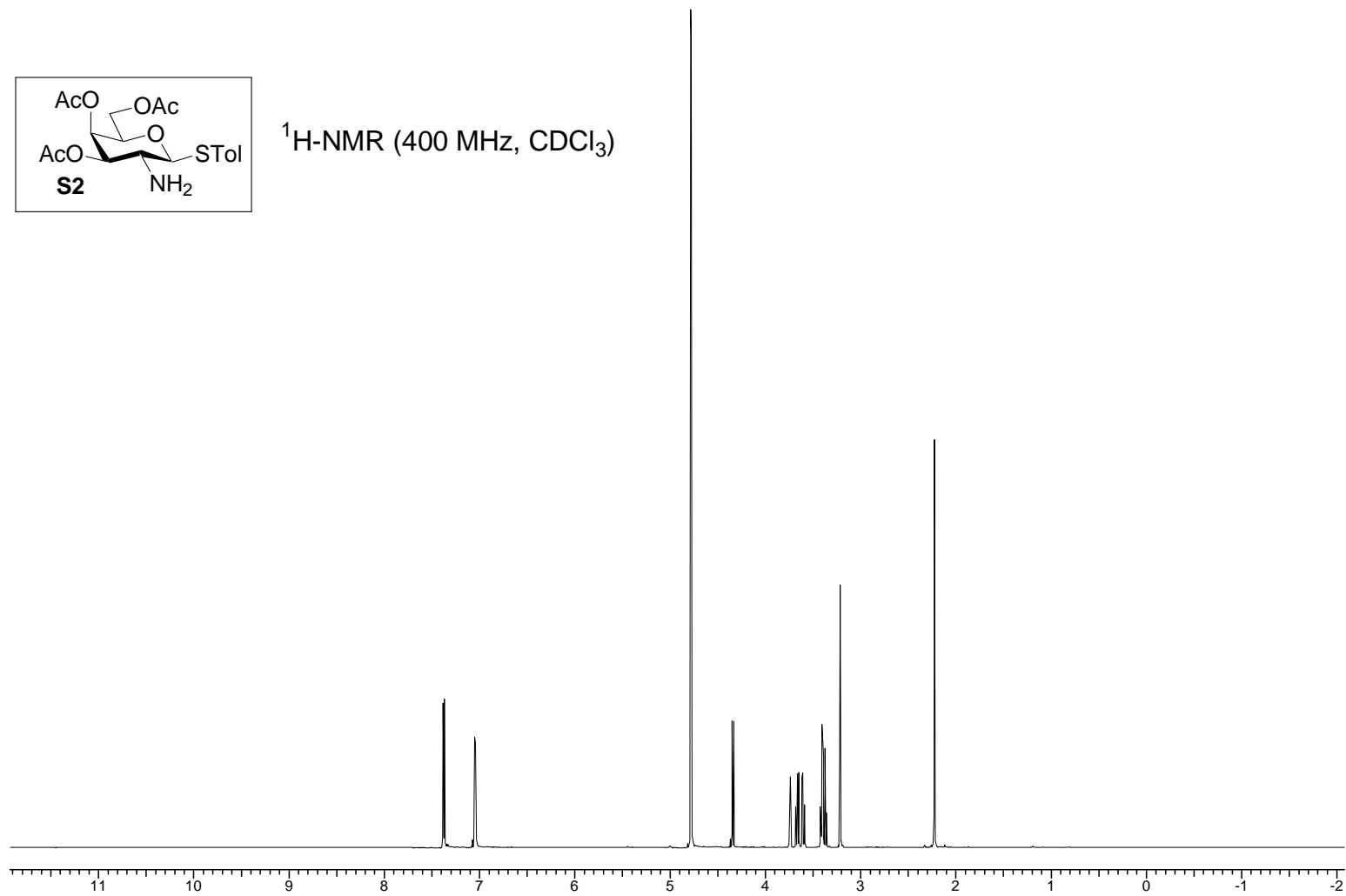
gCOSY(600 MHz, CDCl<sub>3</sub>)

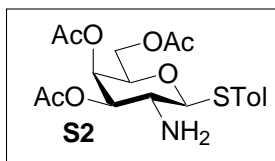




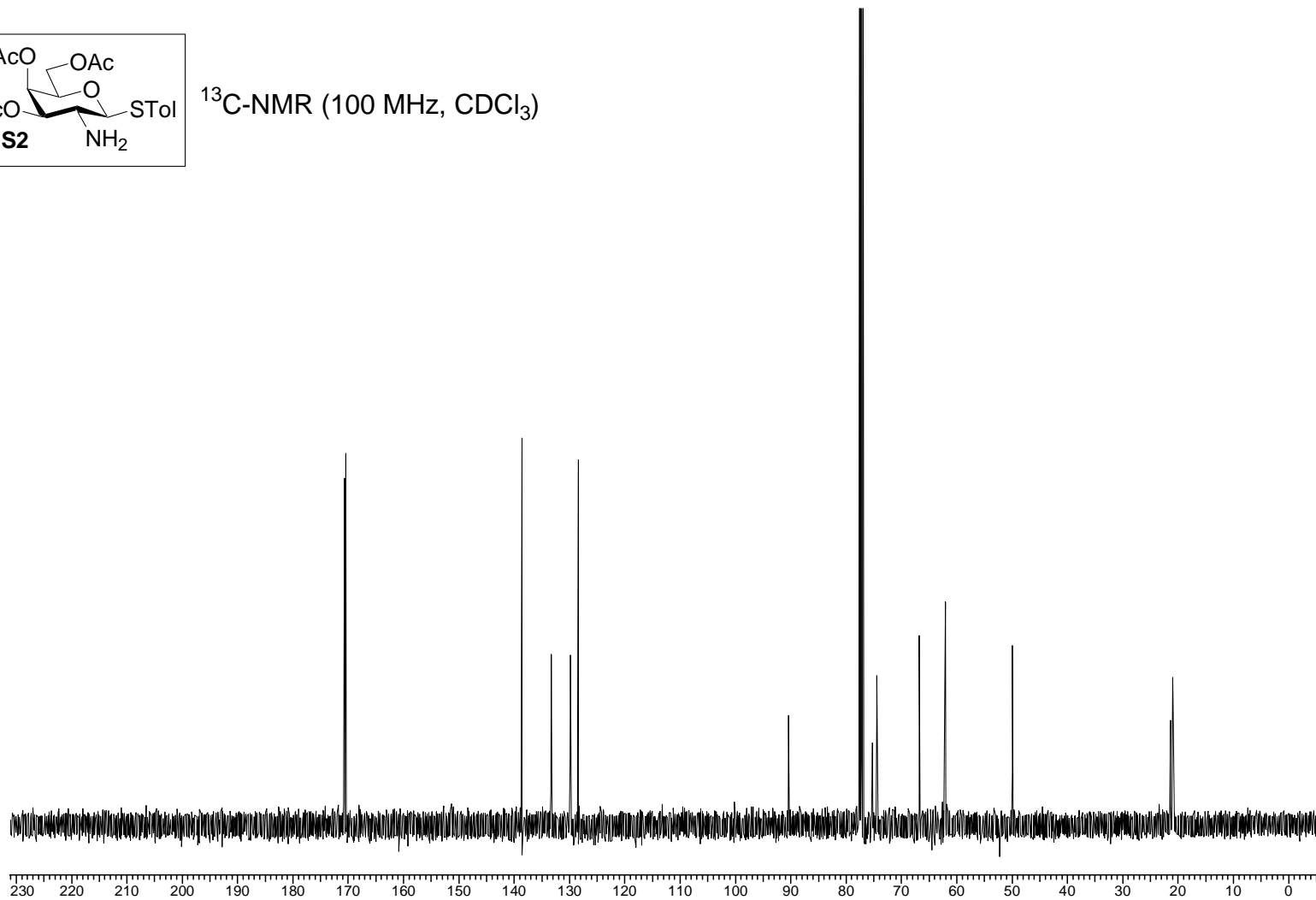


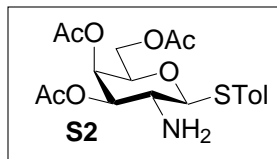
$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )



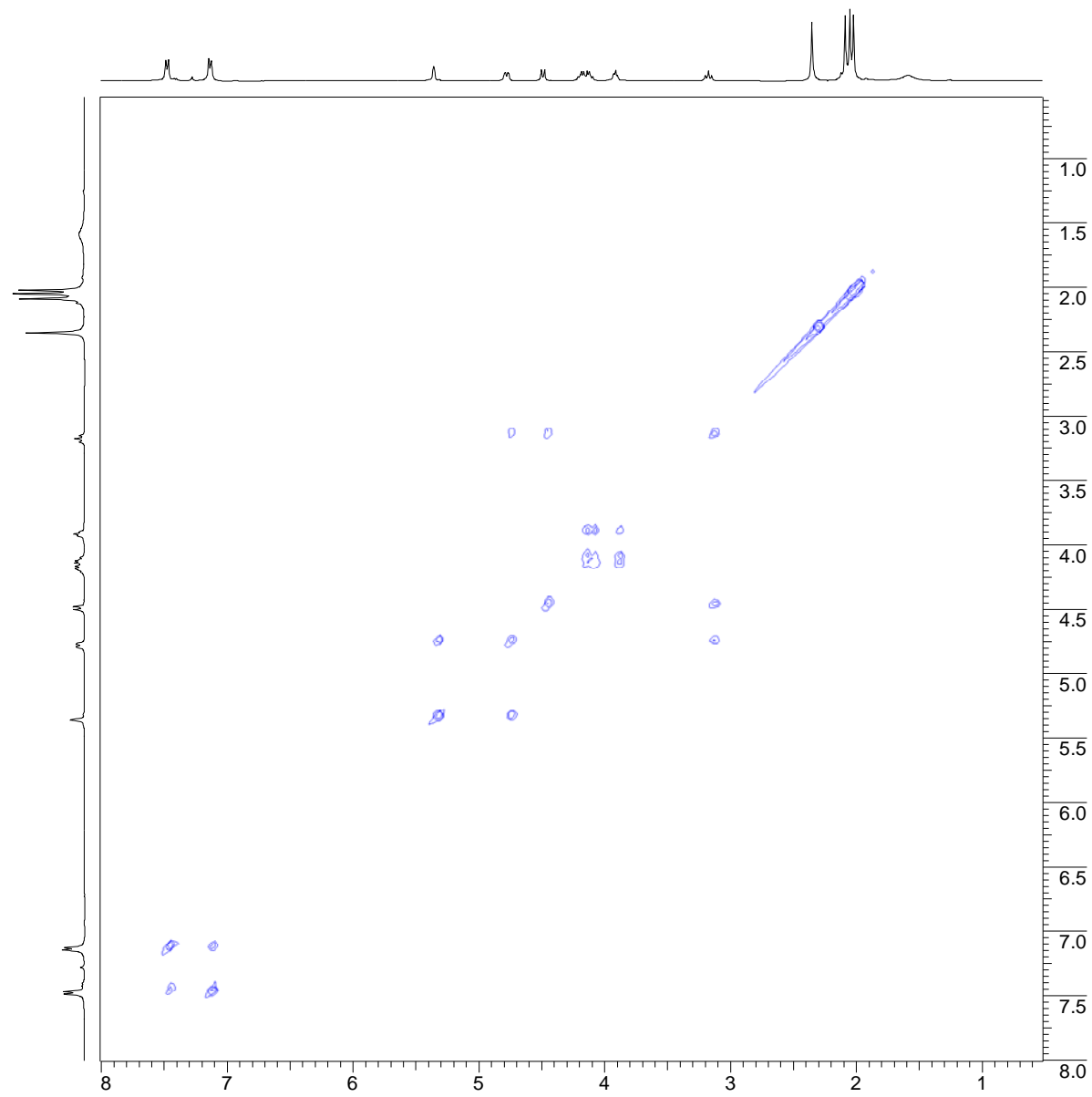


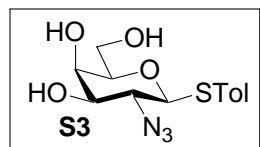
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )



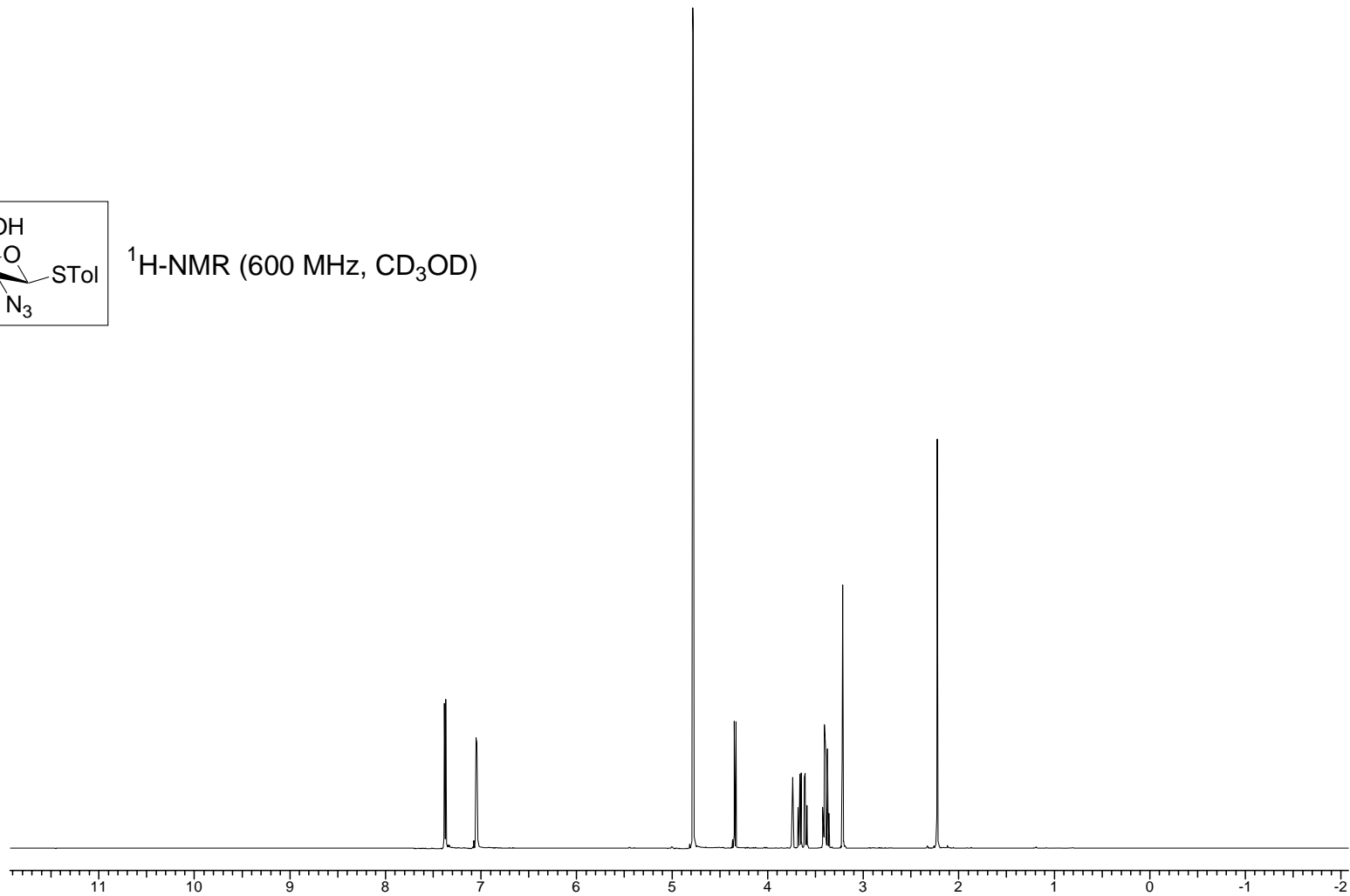


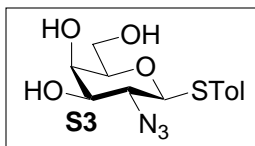
gCOSY (600 MHz, CDCl<sub>3</sub>)



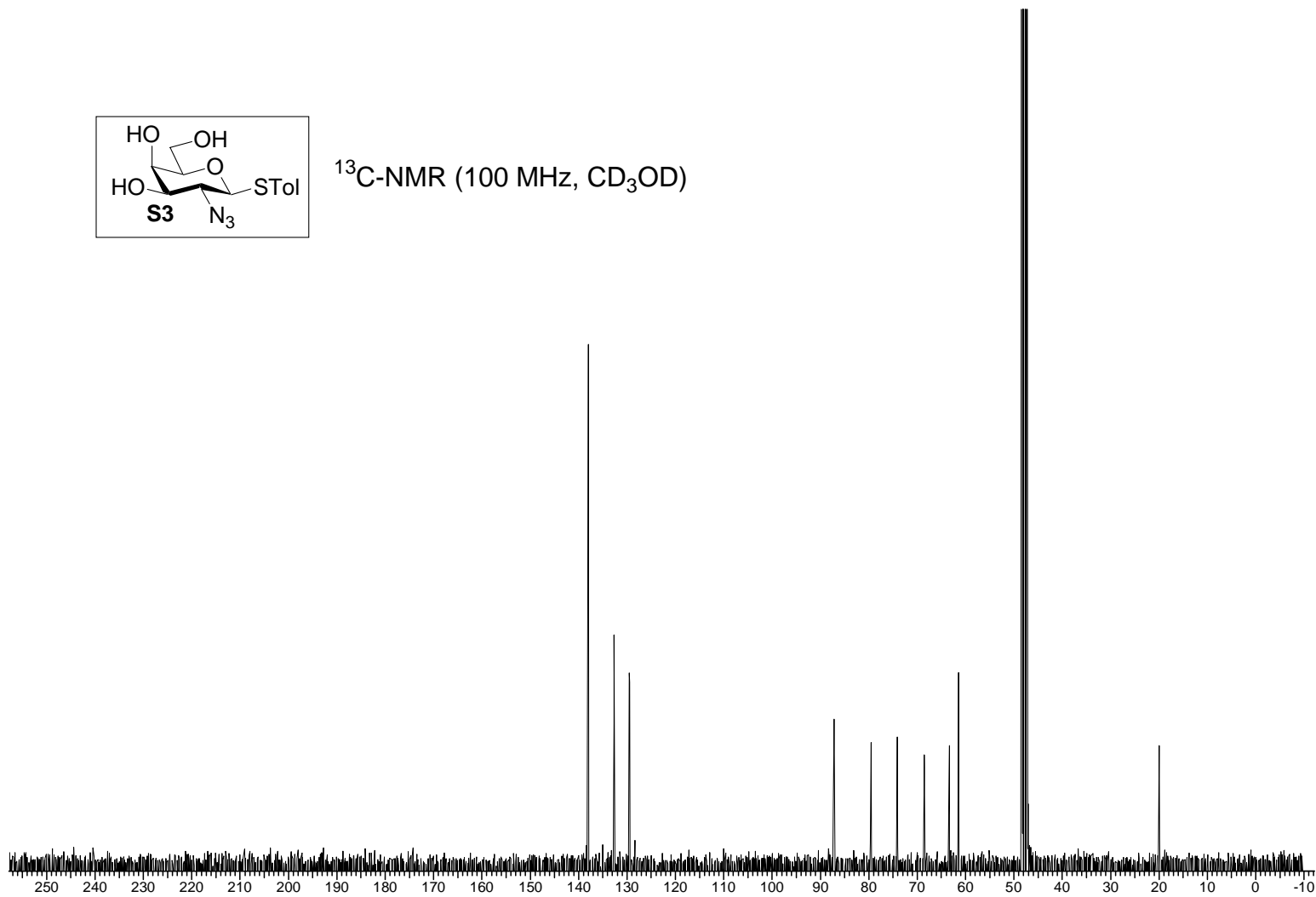


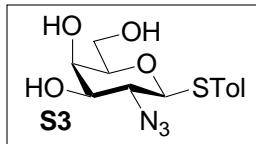
$^1\text{H-NMR}$  (600 MHz,  $\text{CD}_3\text{OD}$ )



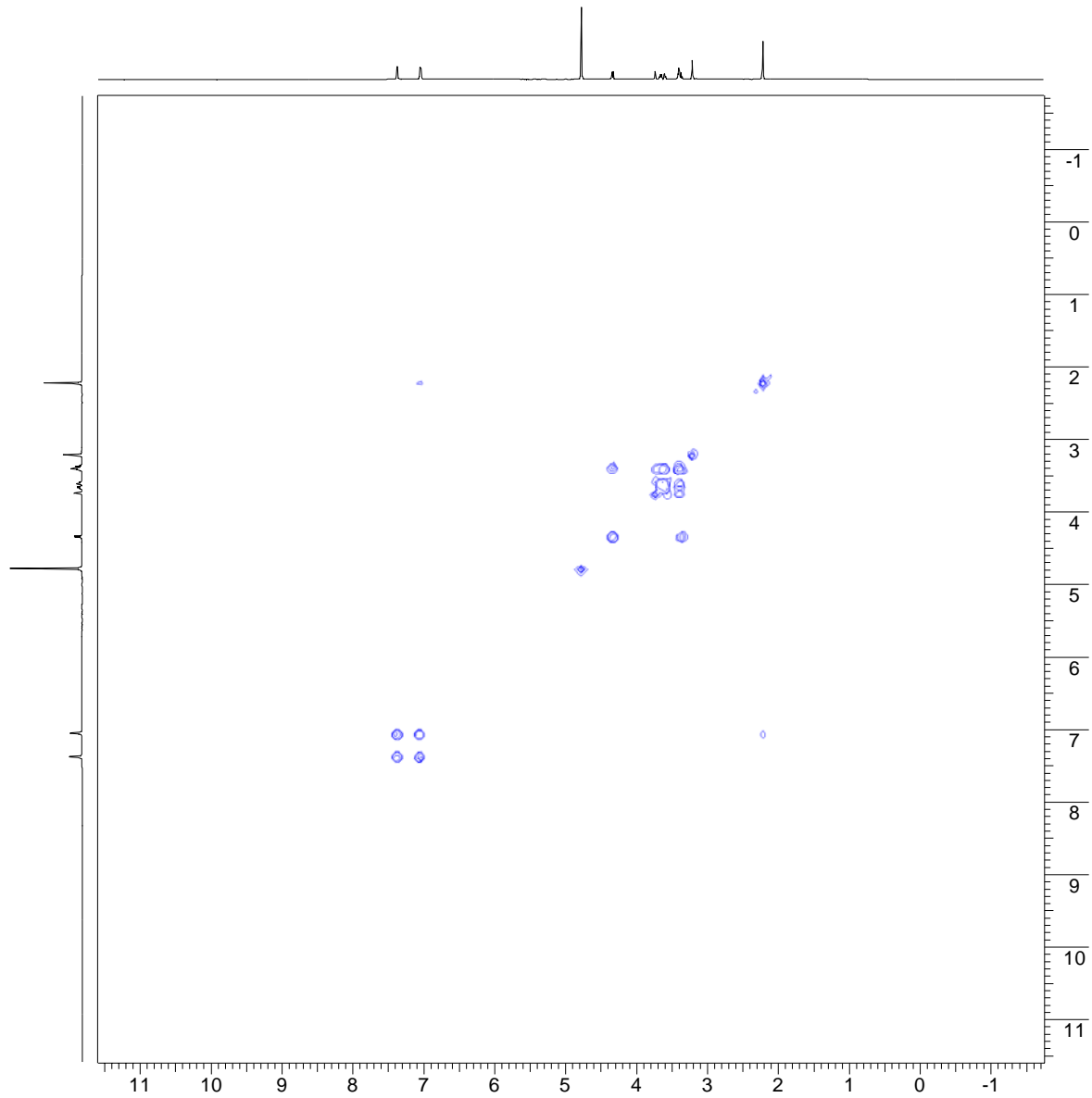


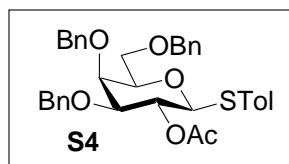
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_3\text{OD}$ )



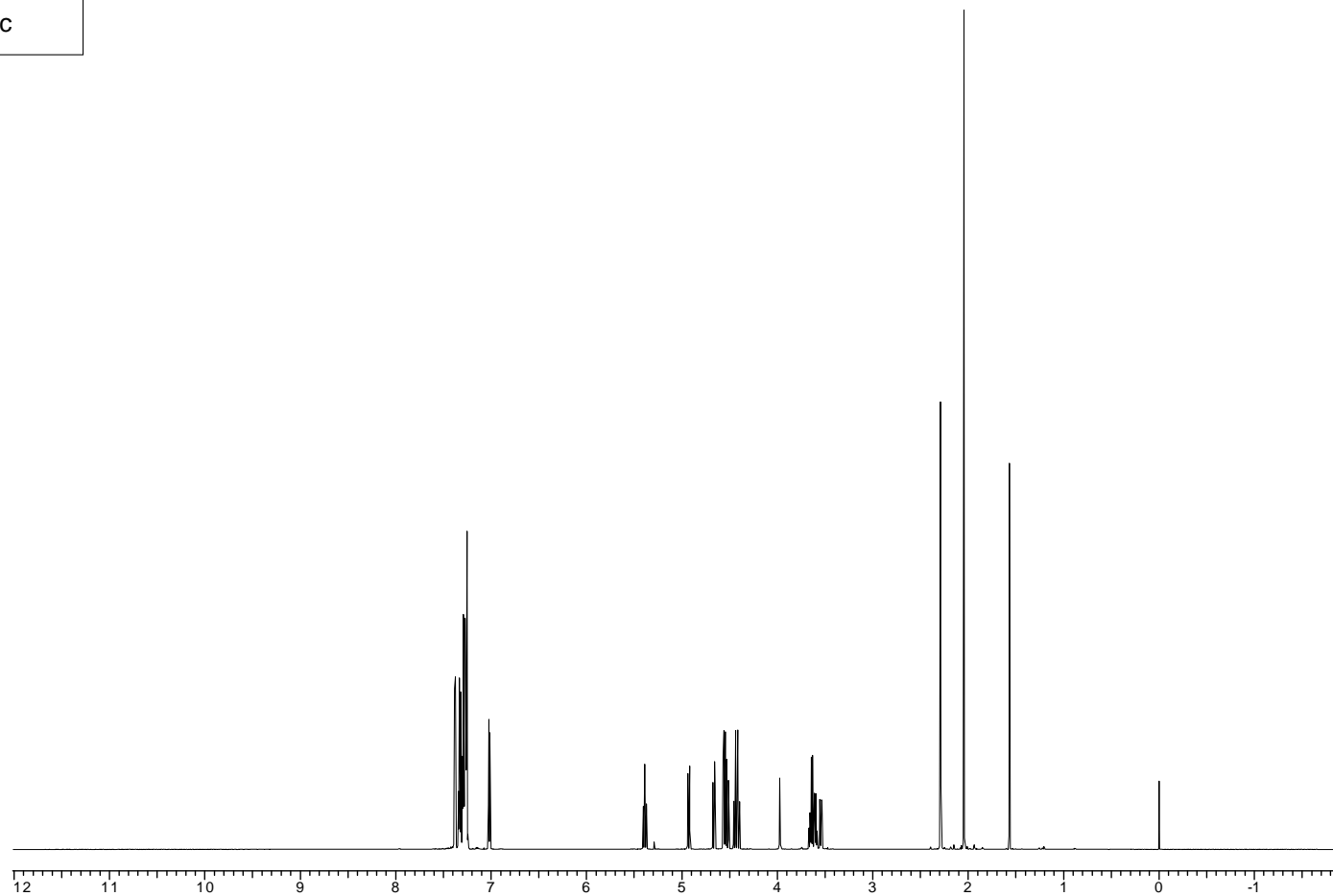


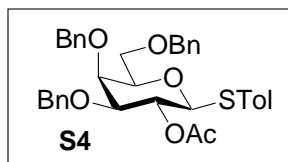
gCOSY (600 MHz, CD<sub>3</sub>OD)



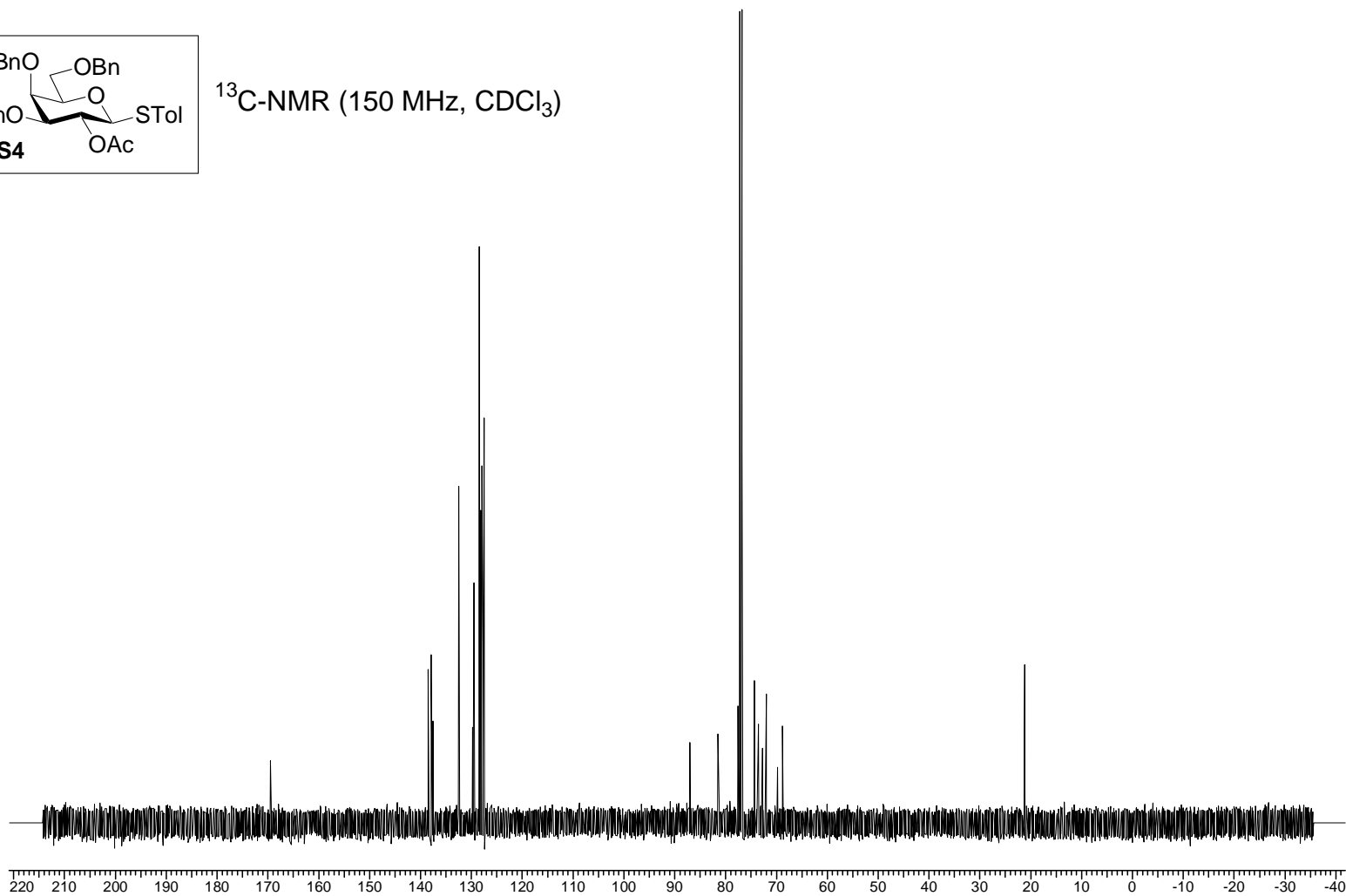


$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

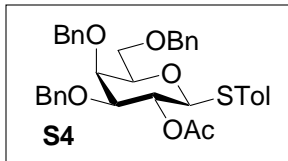




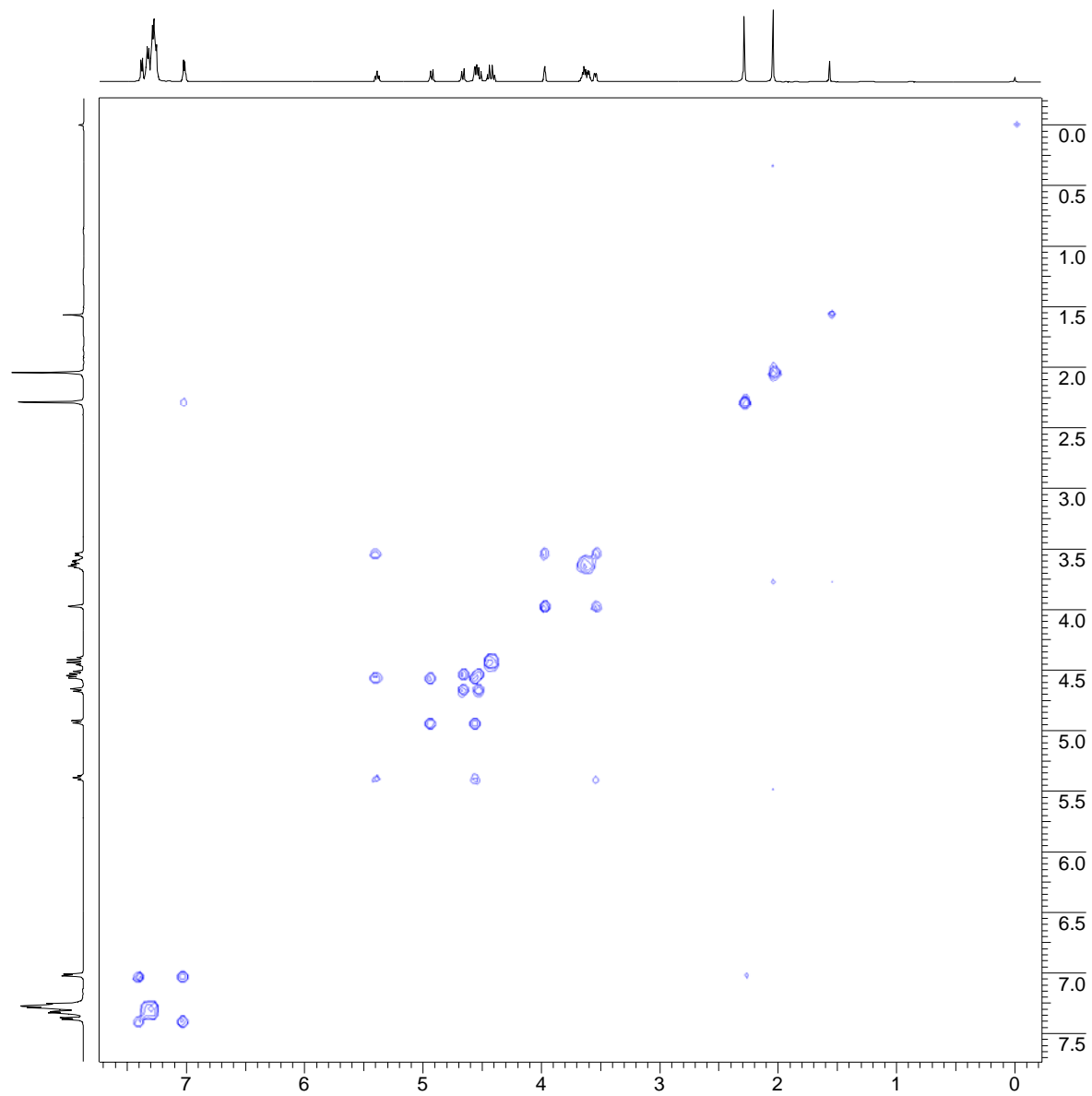
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



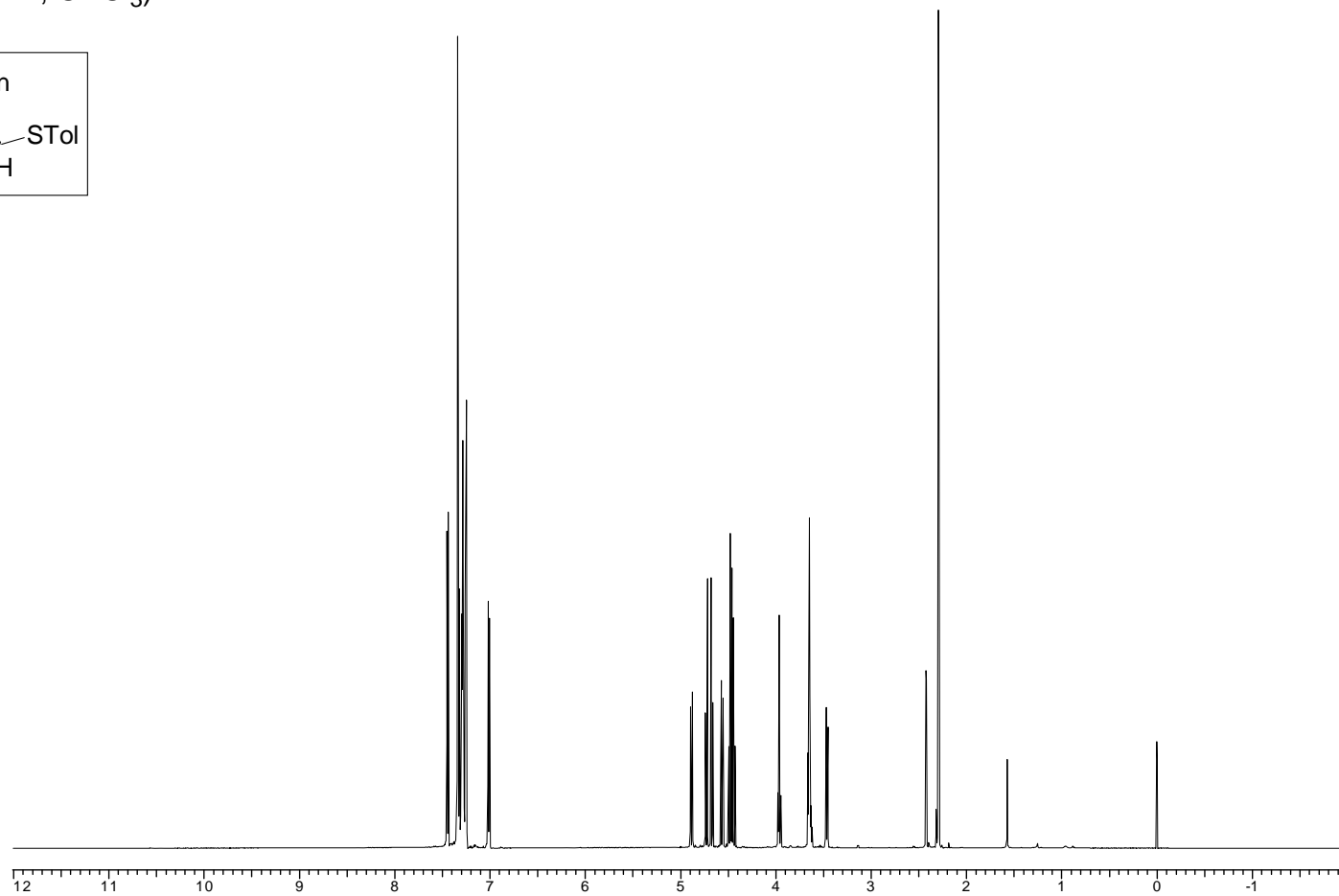
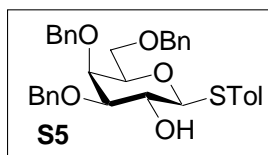




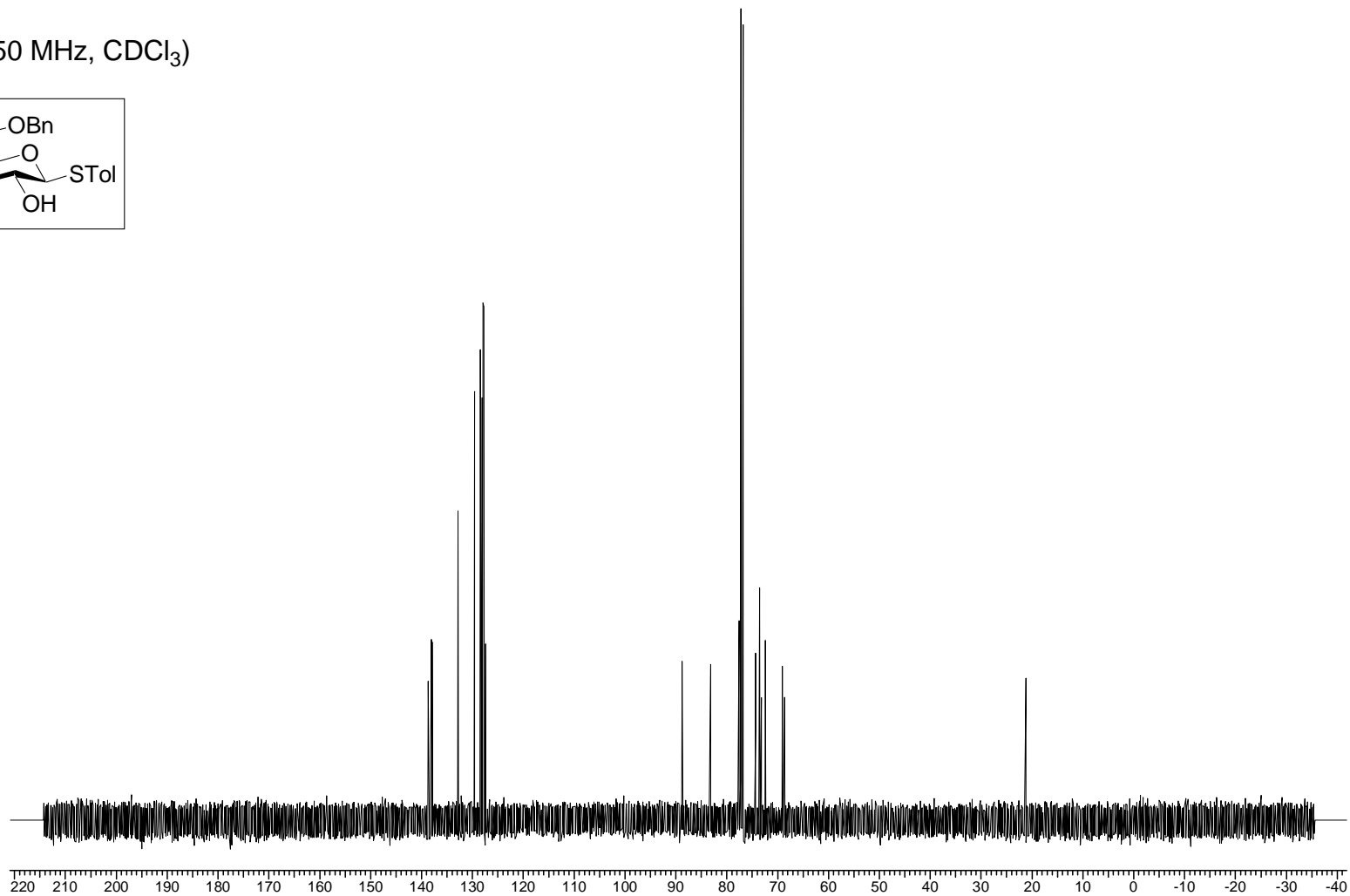
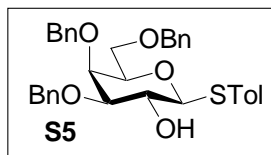
gCOSY (600 MHz, CDCl<sub>3</sub>)



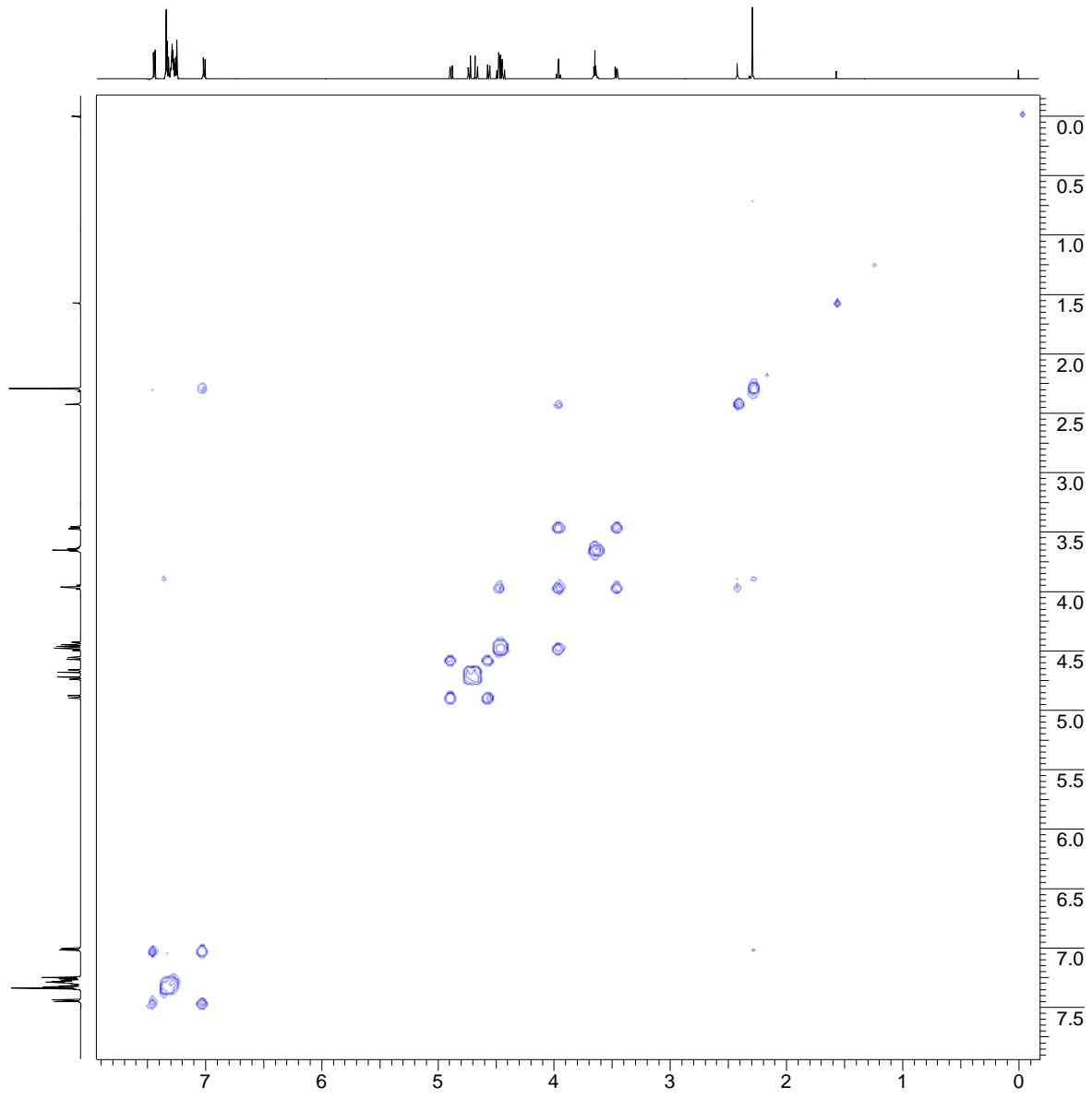
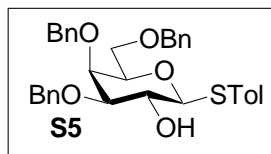
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



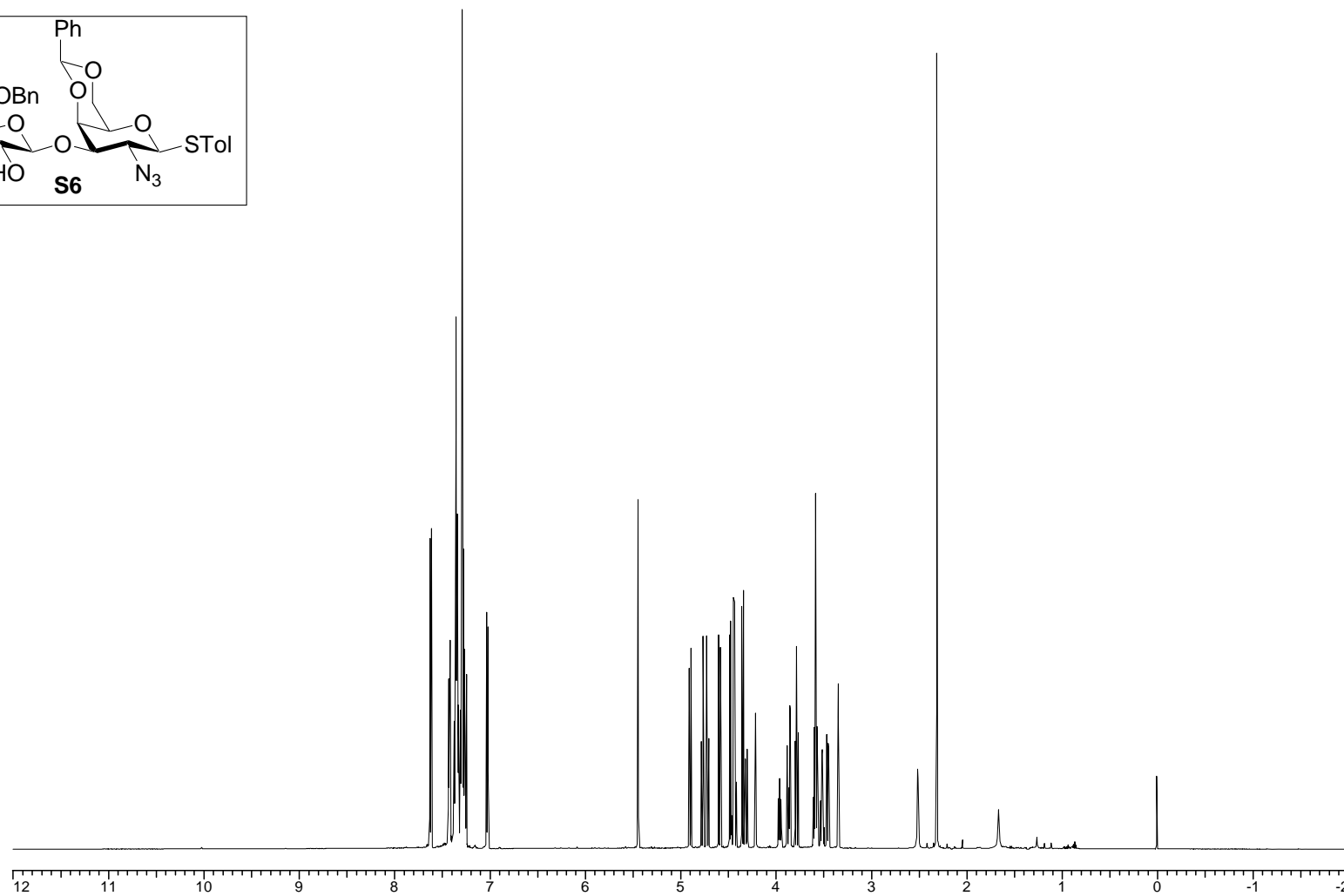
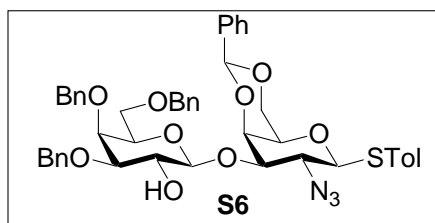
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



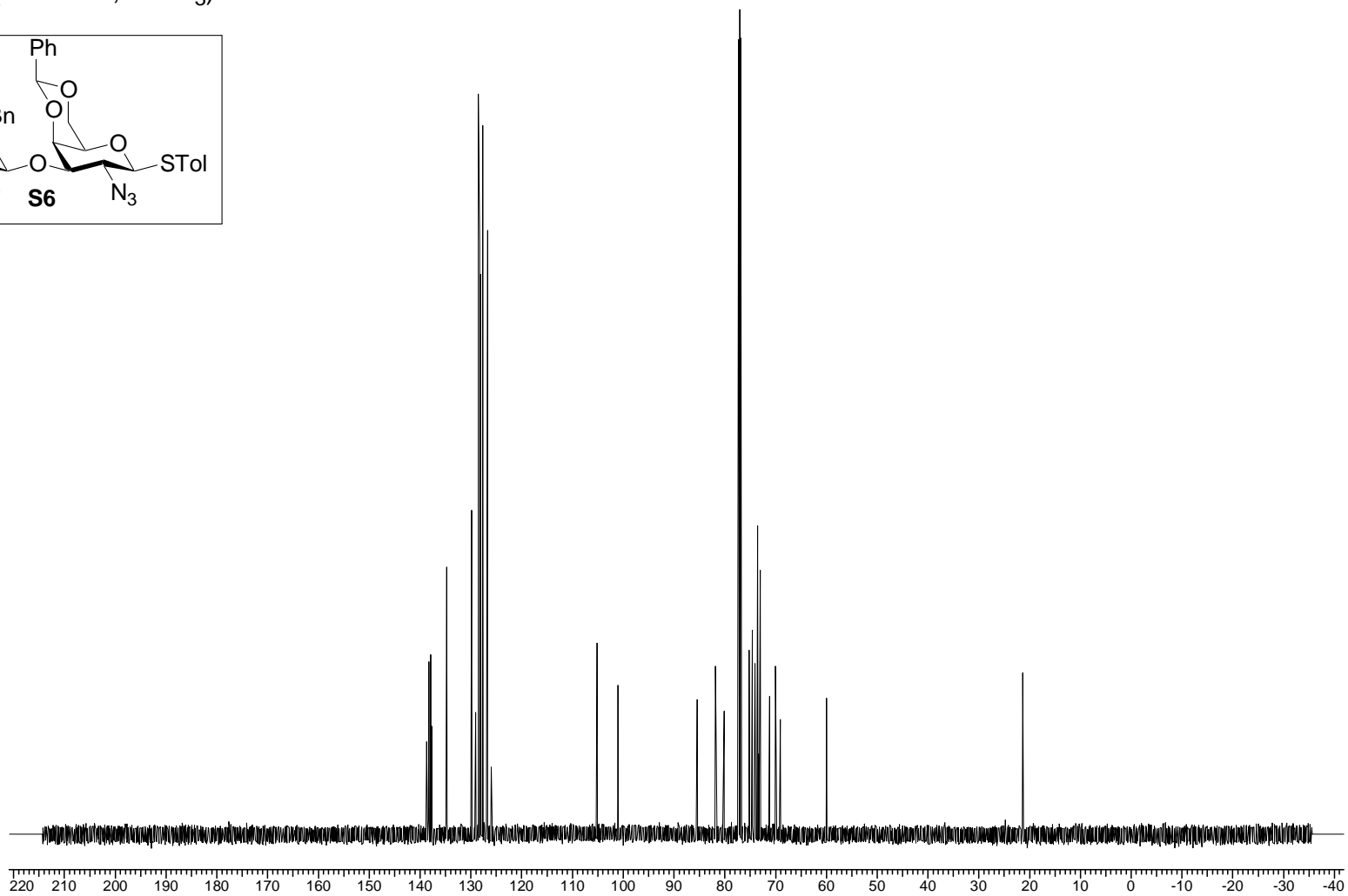
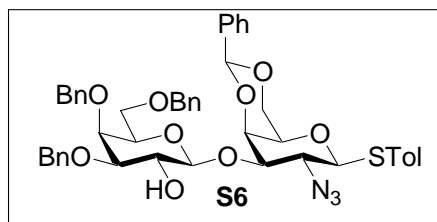
gCOSY (600 MHz, CDCl<sub>3</sub>)



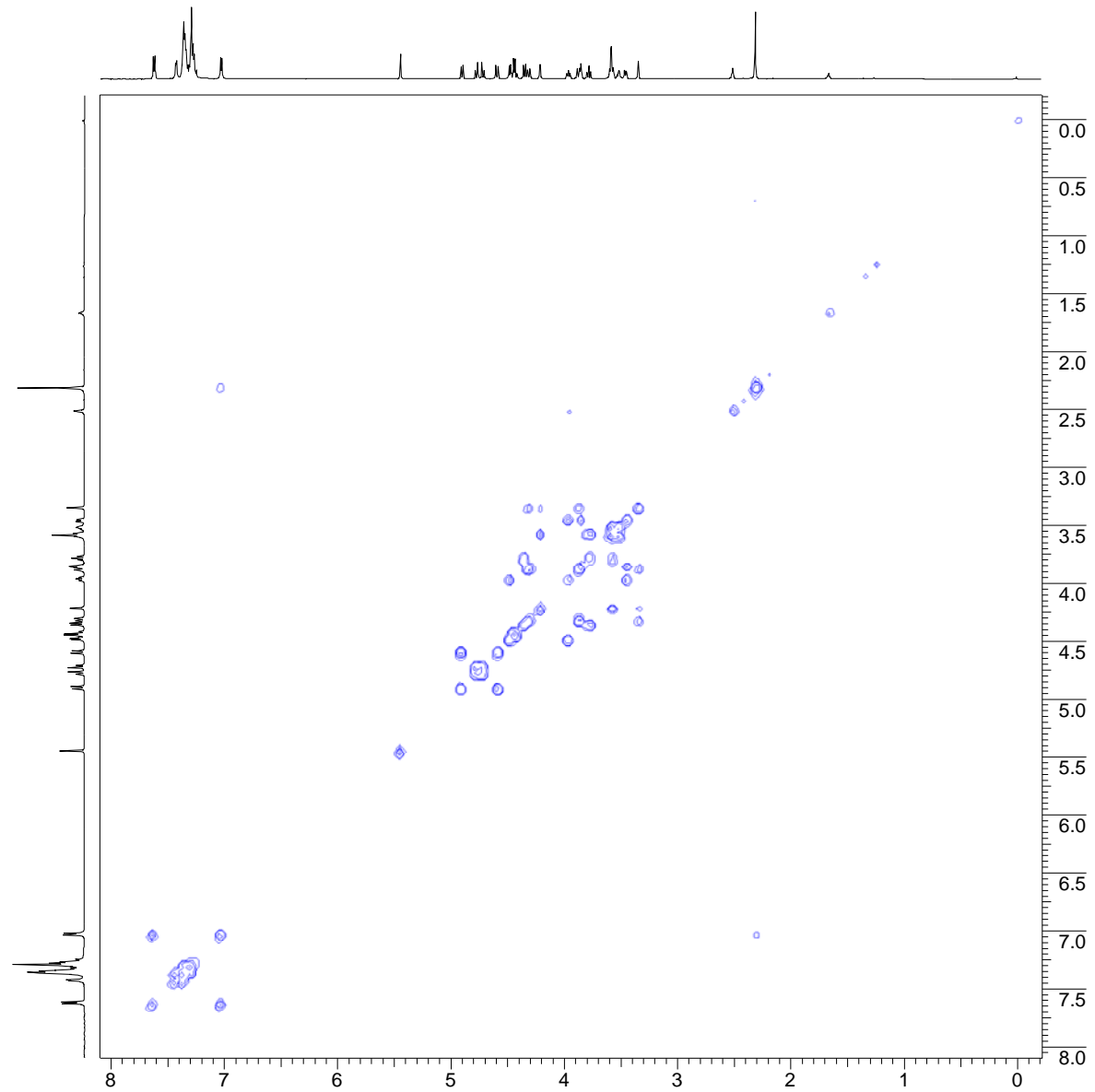
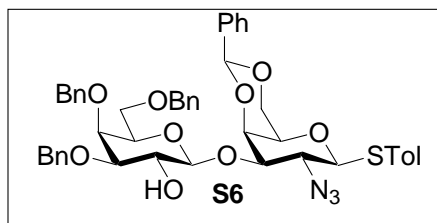
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



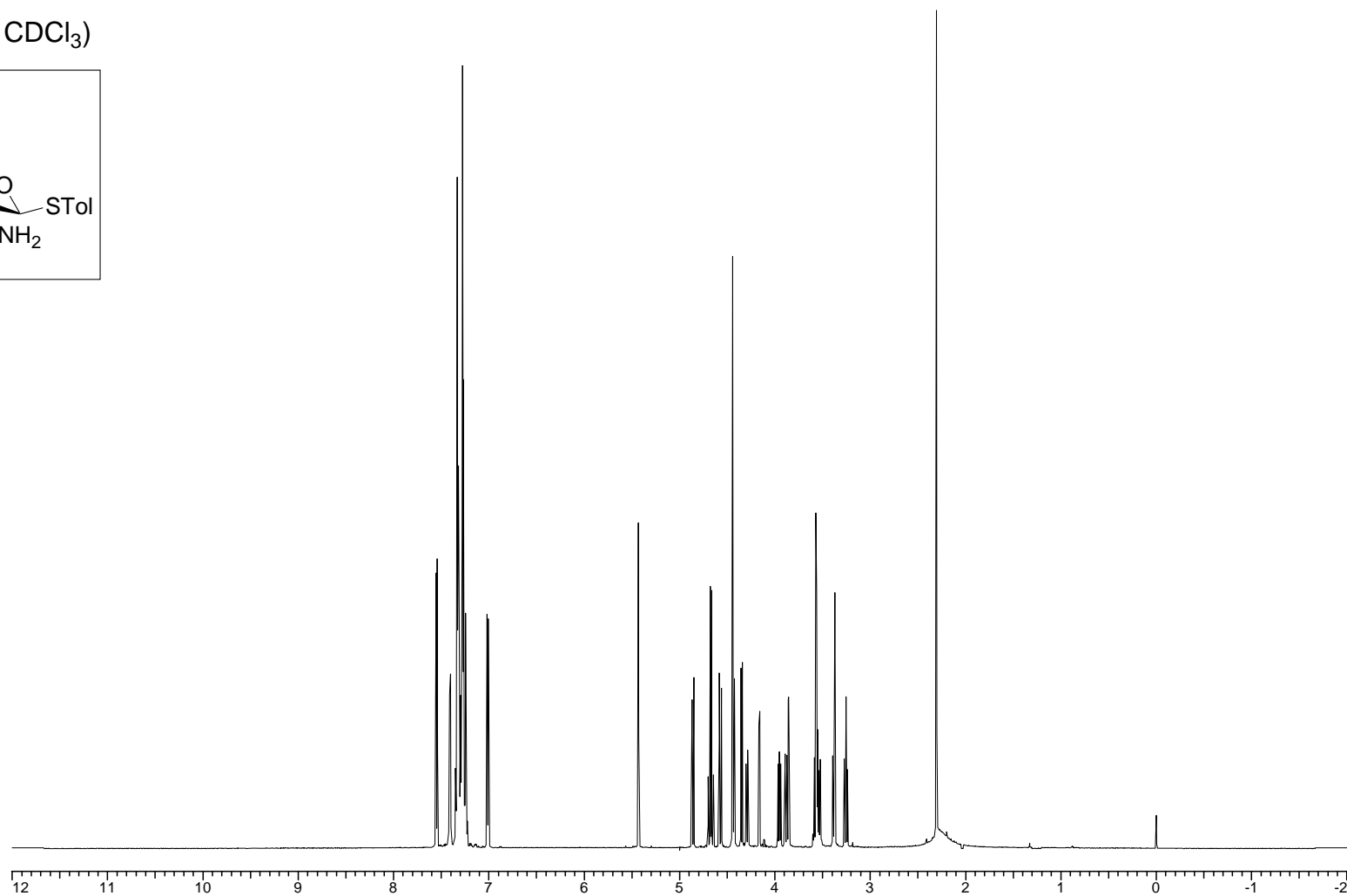
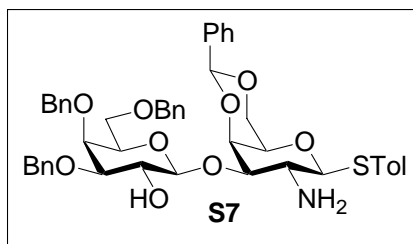
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



gCOSY (600 MHz, CDCl<sub>3</sub>)

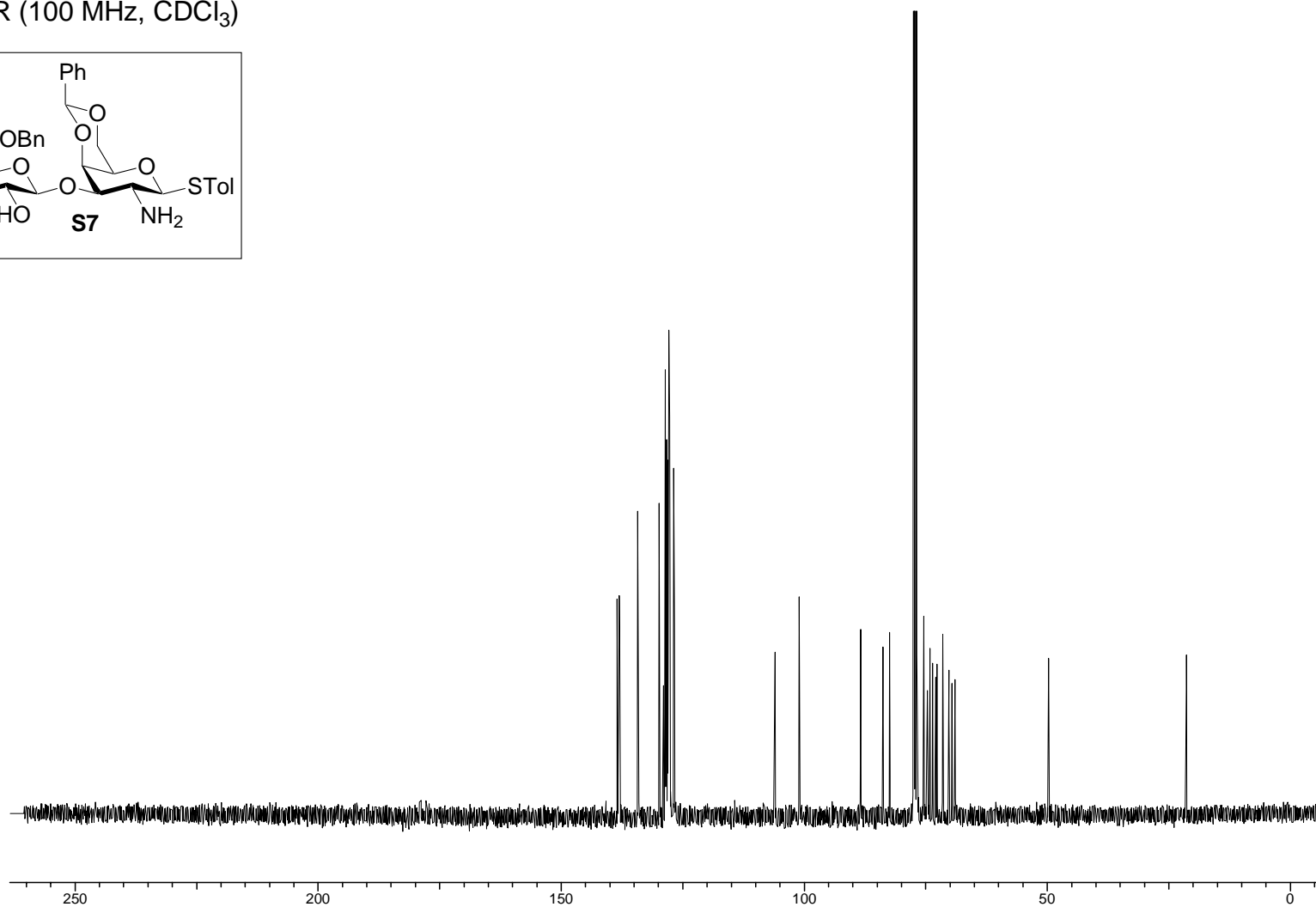
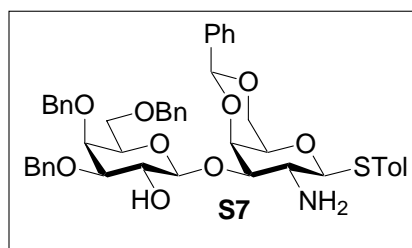


$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

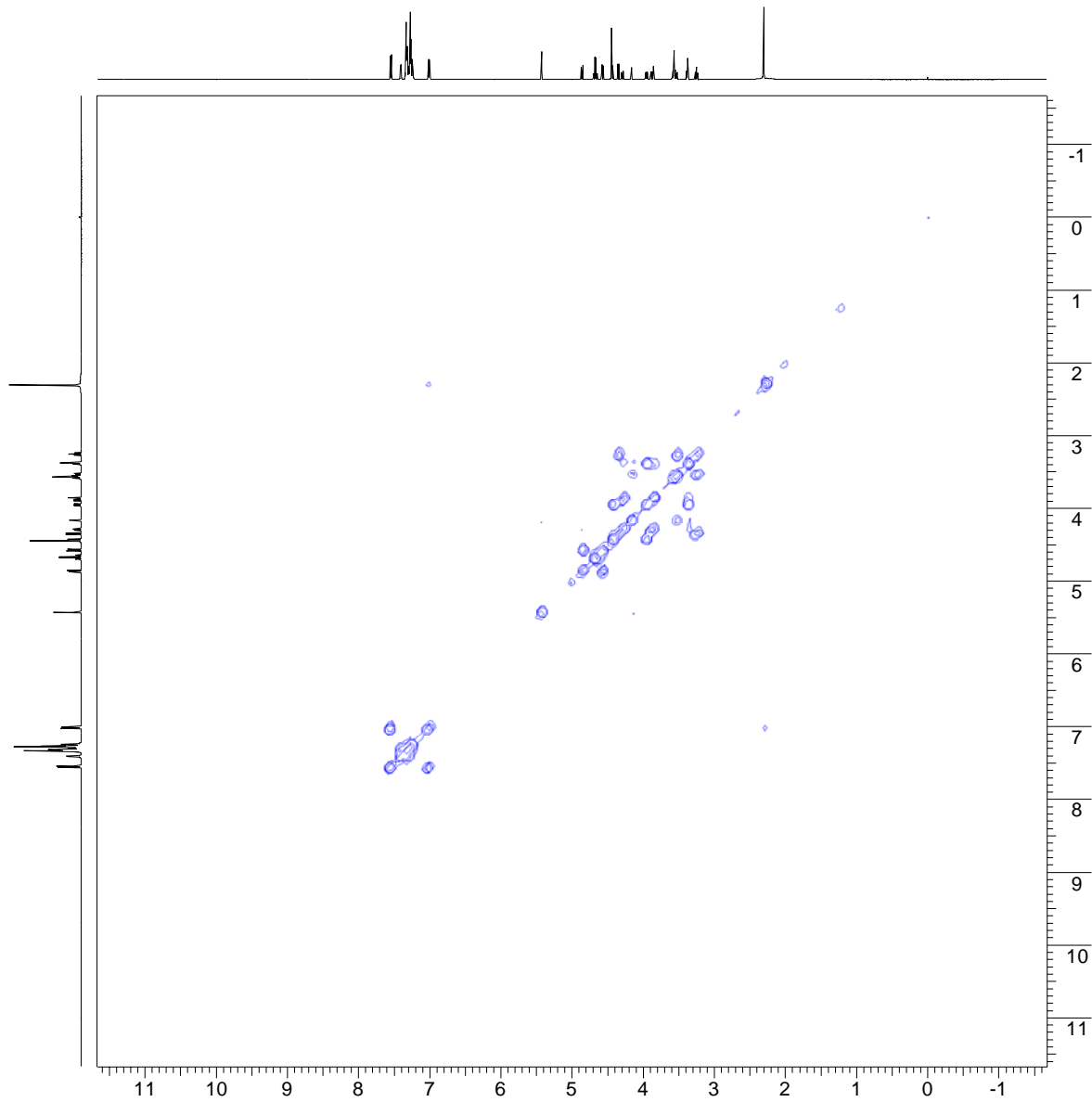
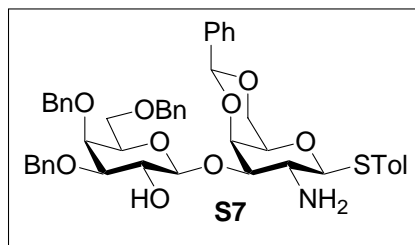




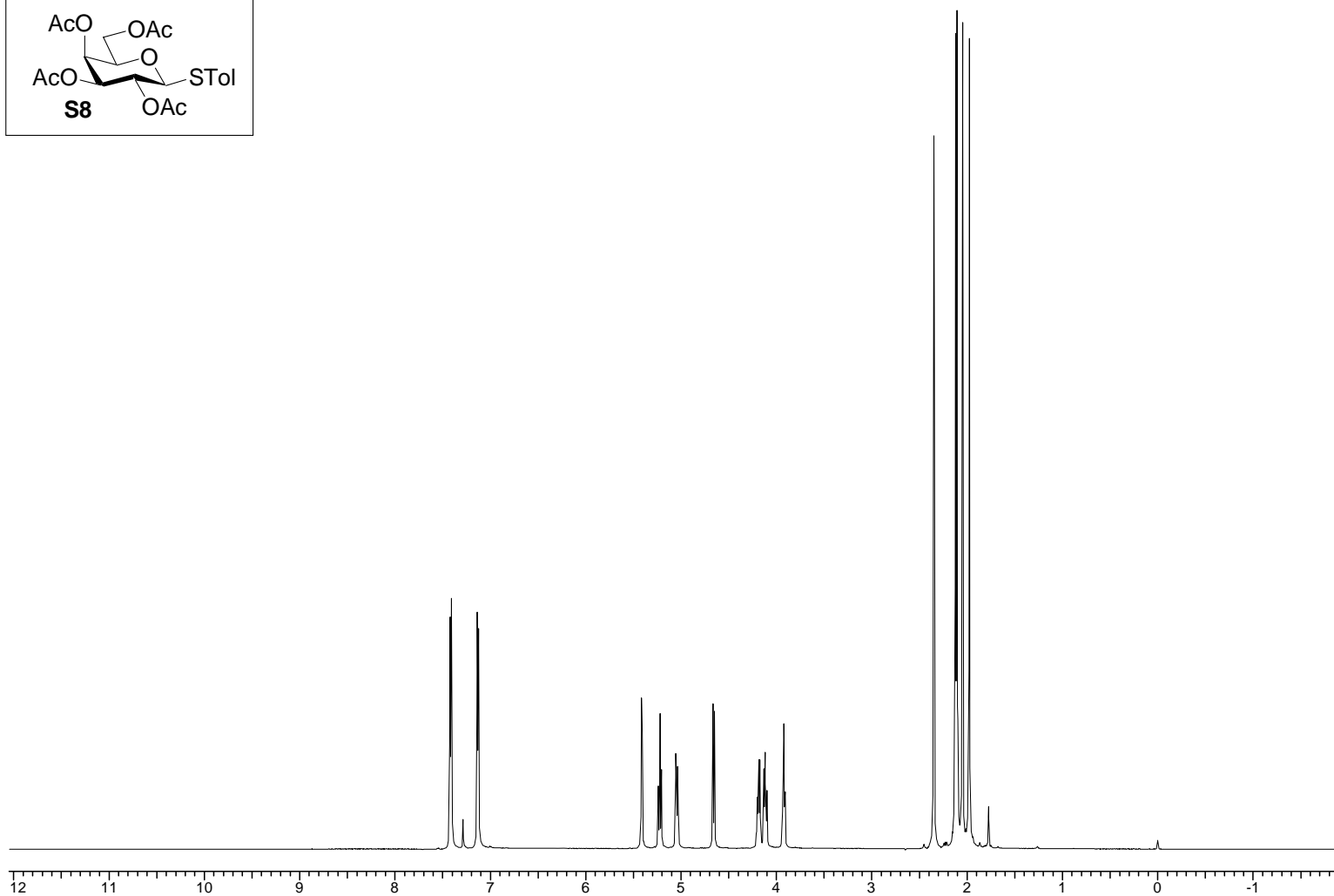
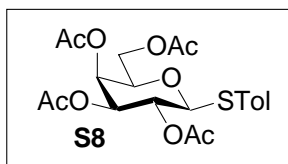
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )



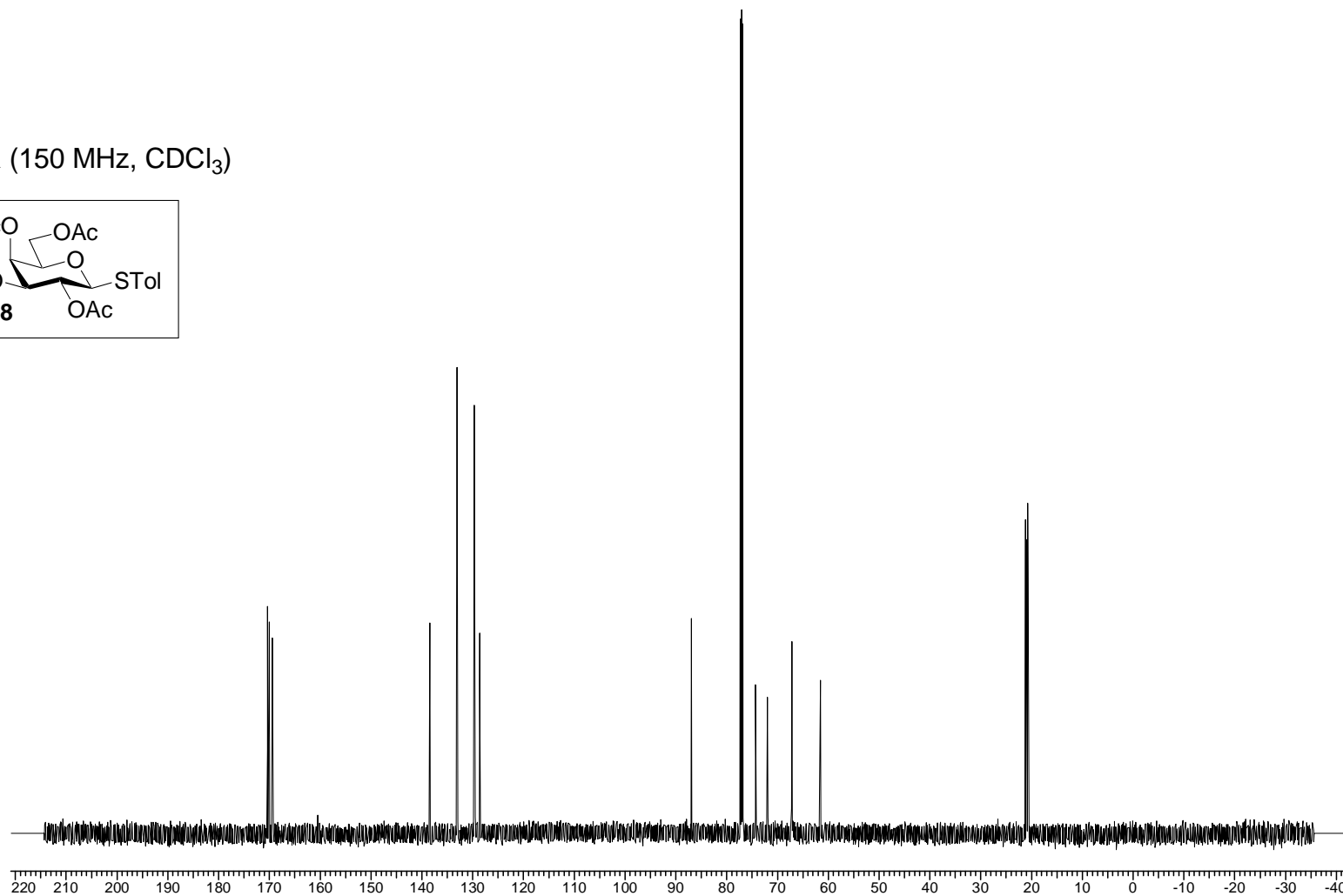
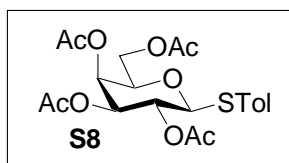
gCOSY (600 MHz, CDCl<sub>3</sub>)



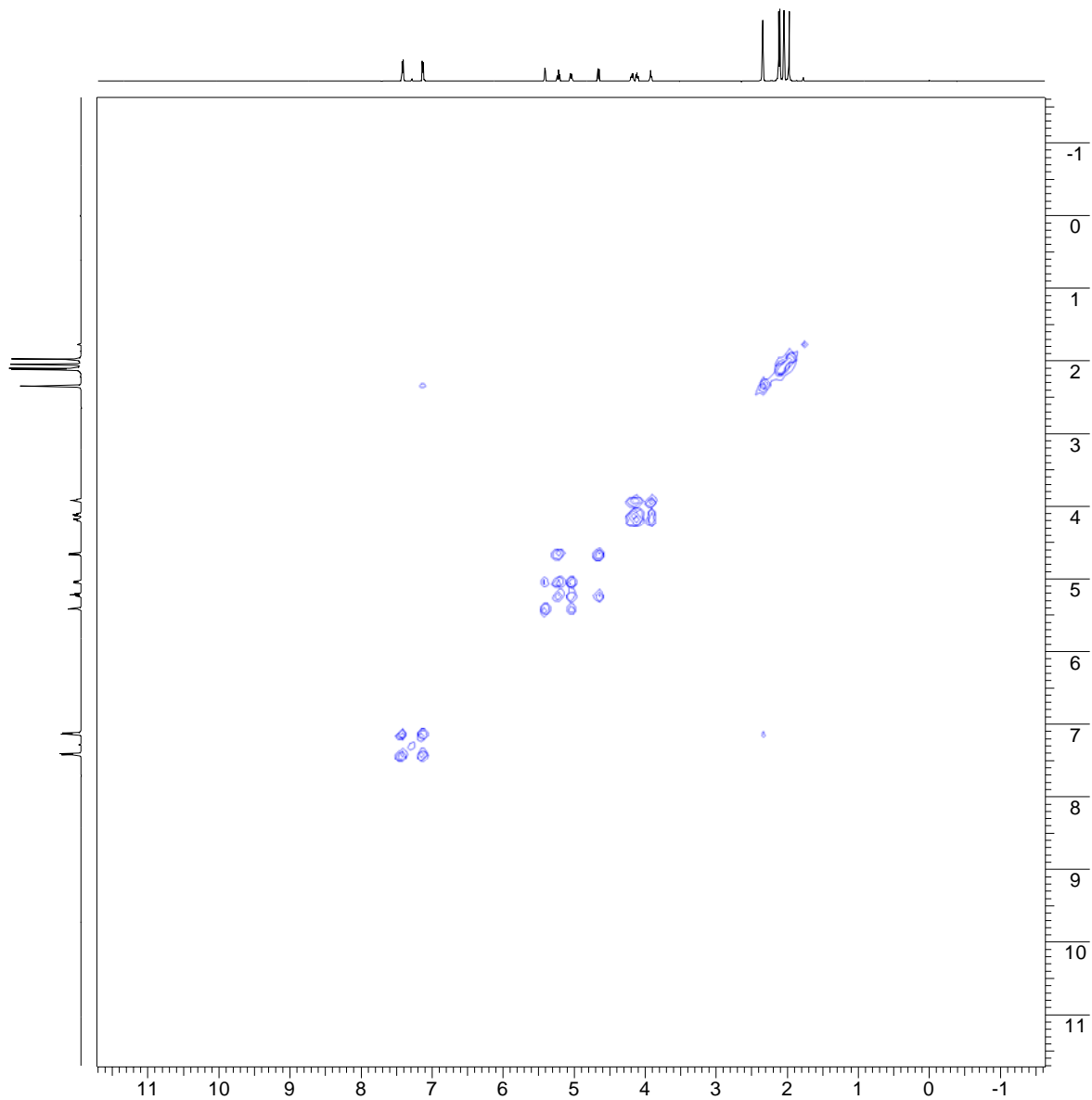
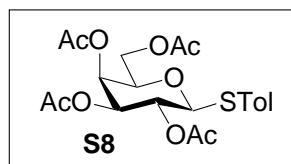
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



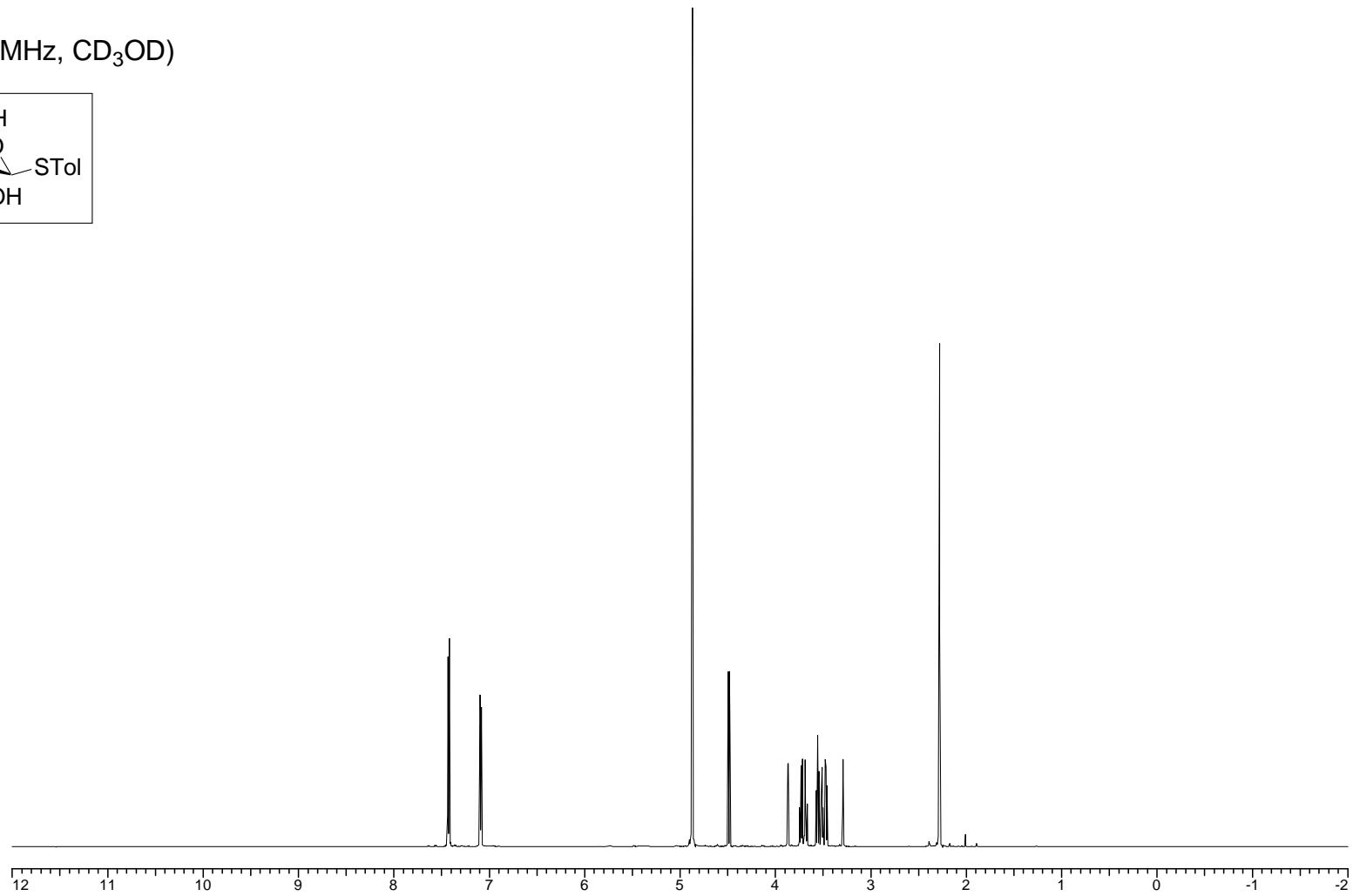
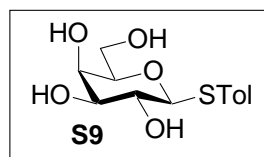
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



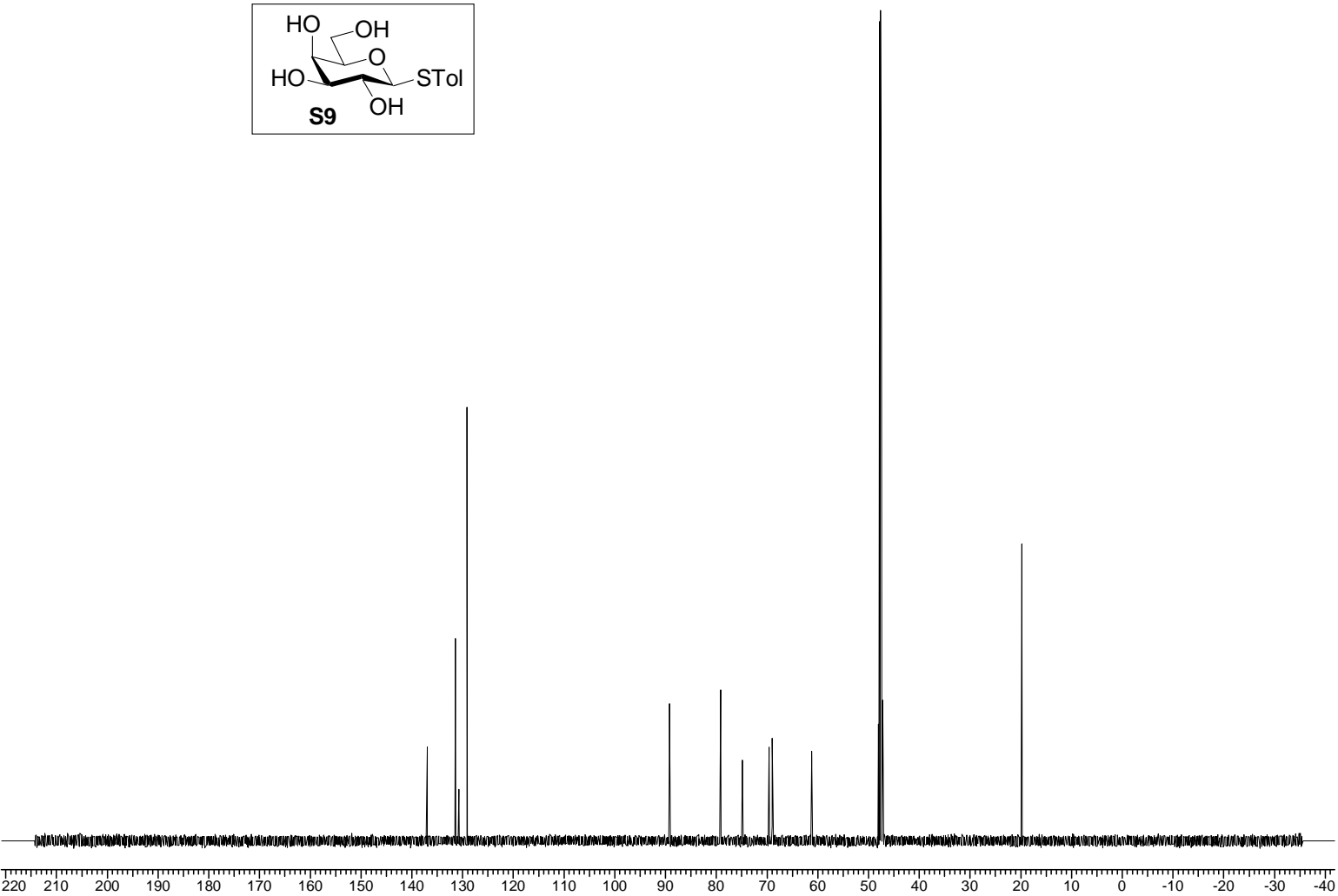
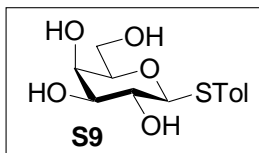
gCOSY(600 MHz, CDCl<sub>3</sub>)



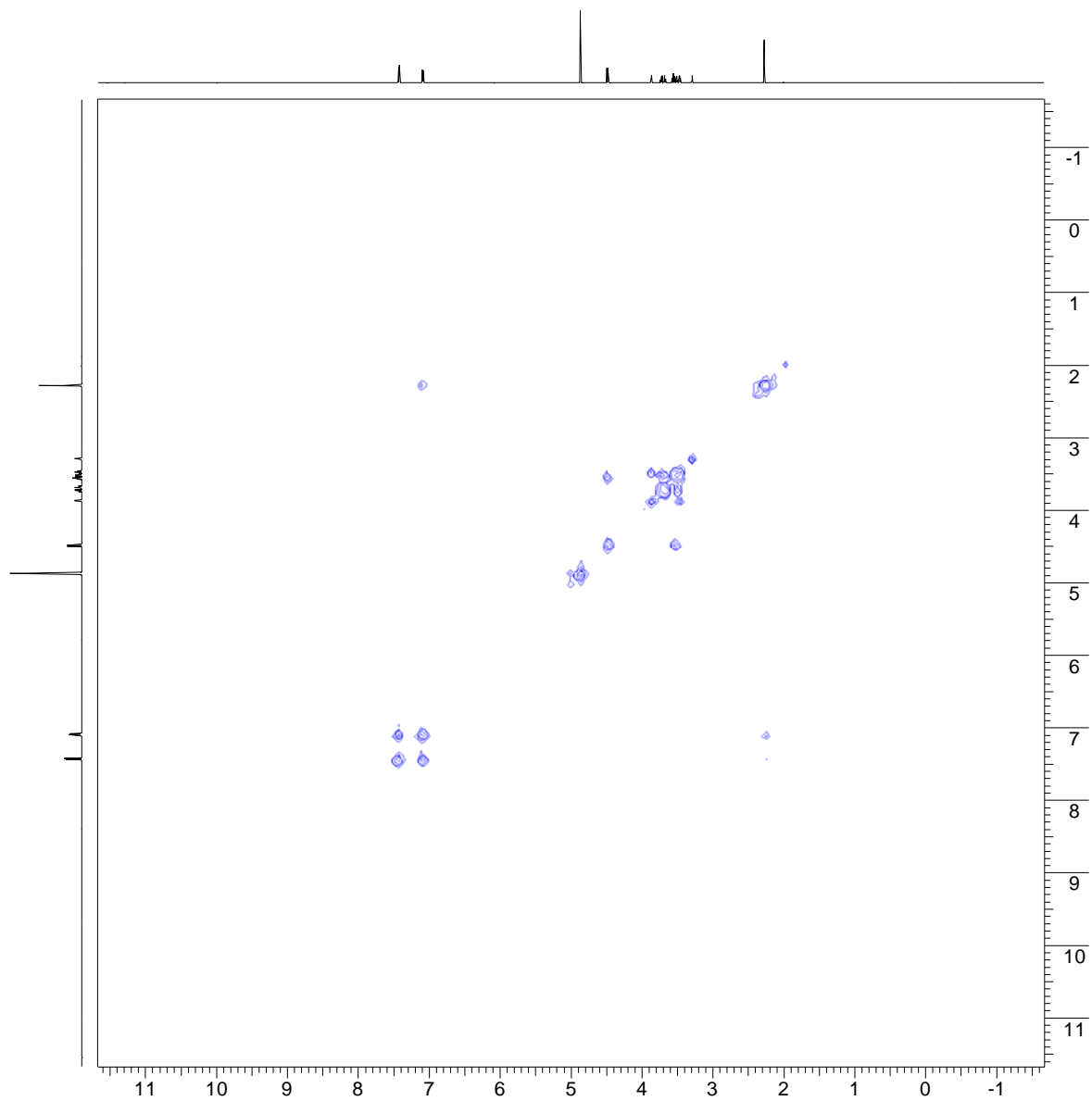
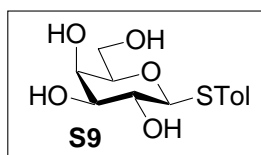
$^1\text{H-NMR}$  (600 MHz,  $\text{CD}_3\text{OD}$ )



$^{13}\text{C}$ -NMR (150 MHz,  $\text{CD}_3\text{OD}$ )

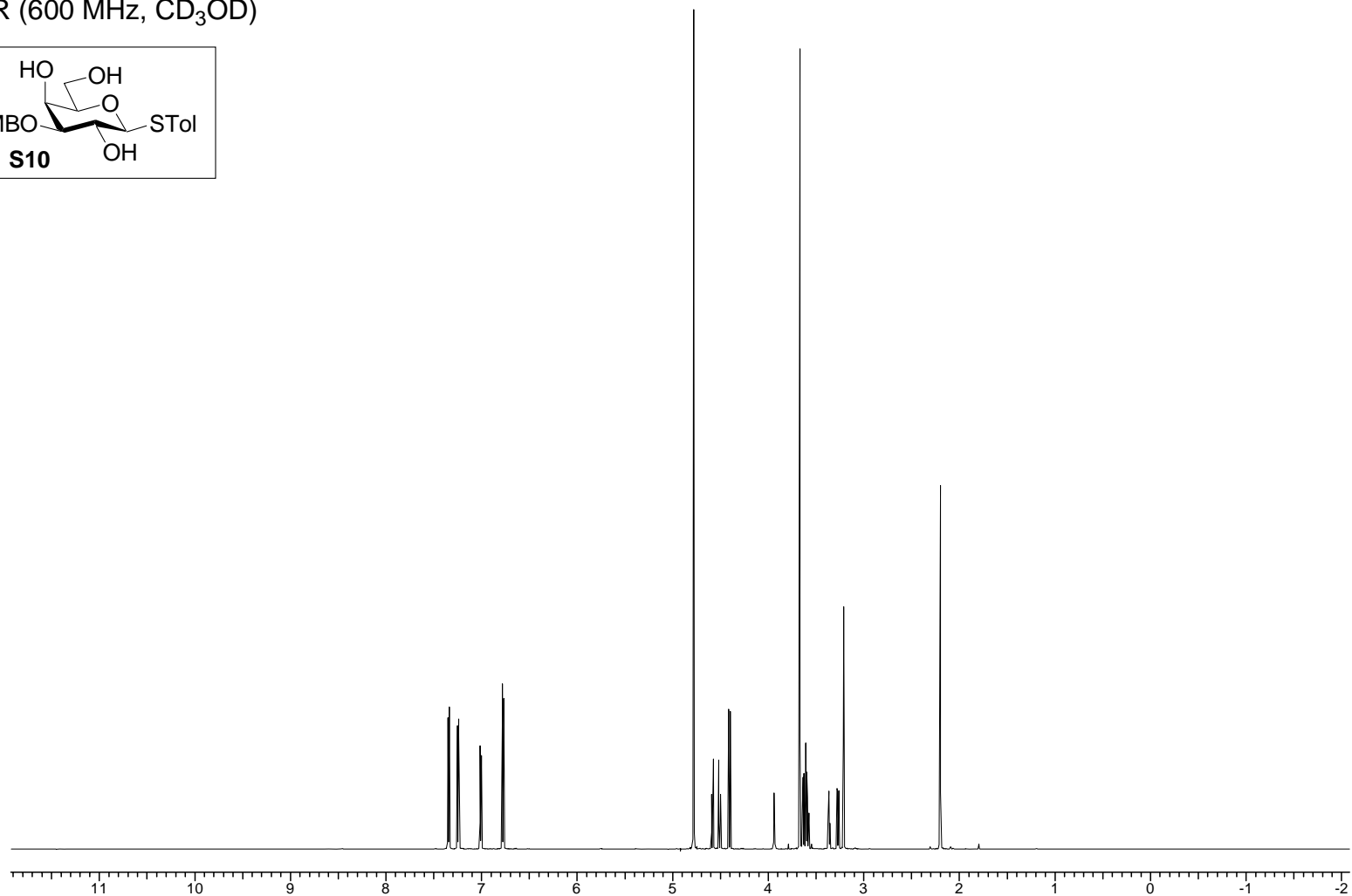
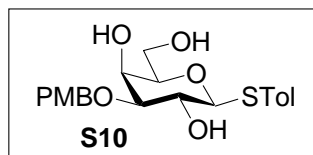


gCOSY (600 MHz, CD<sub>3</sub>OD)

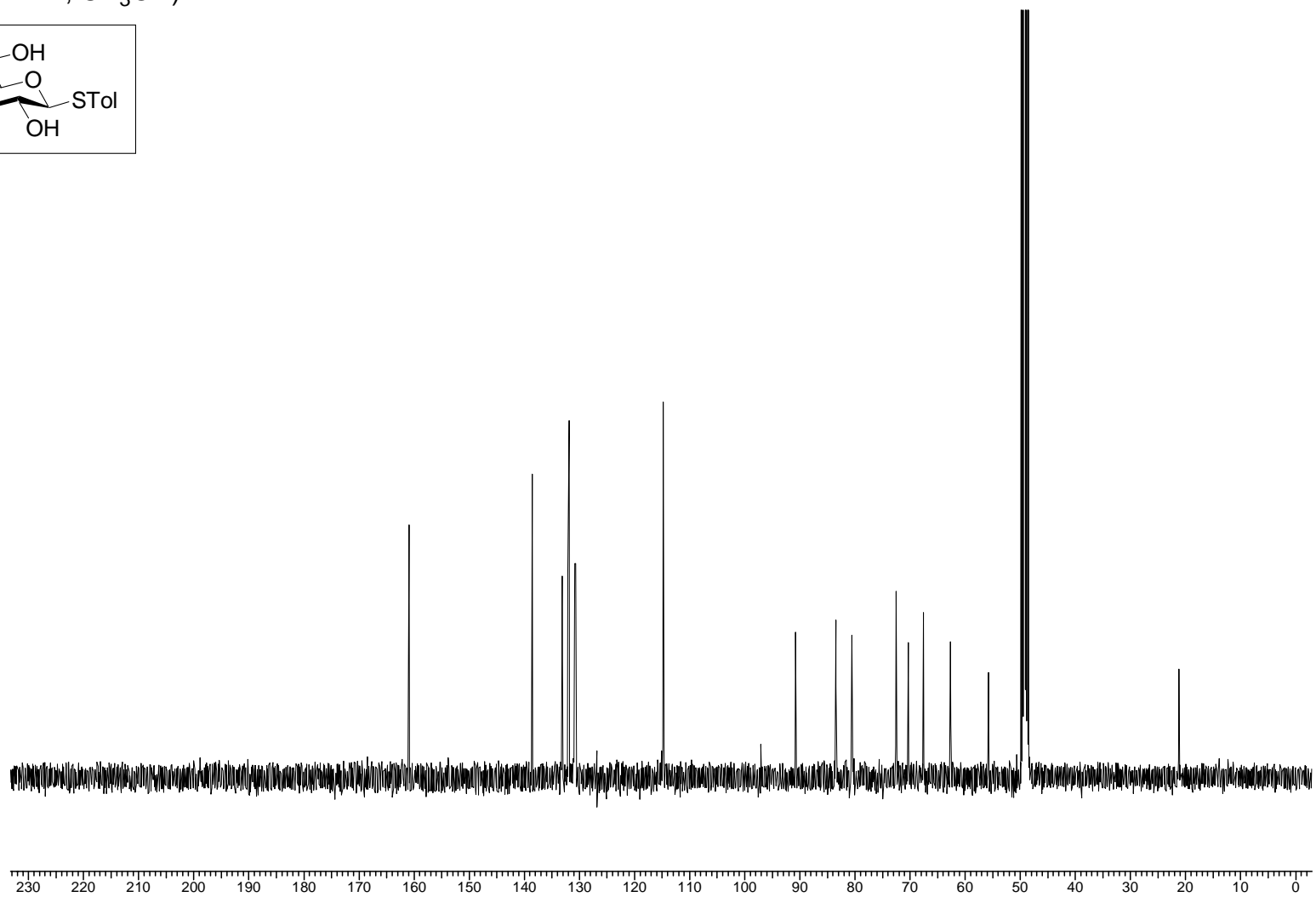
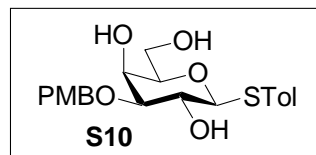




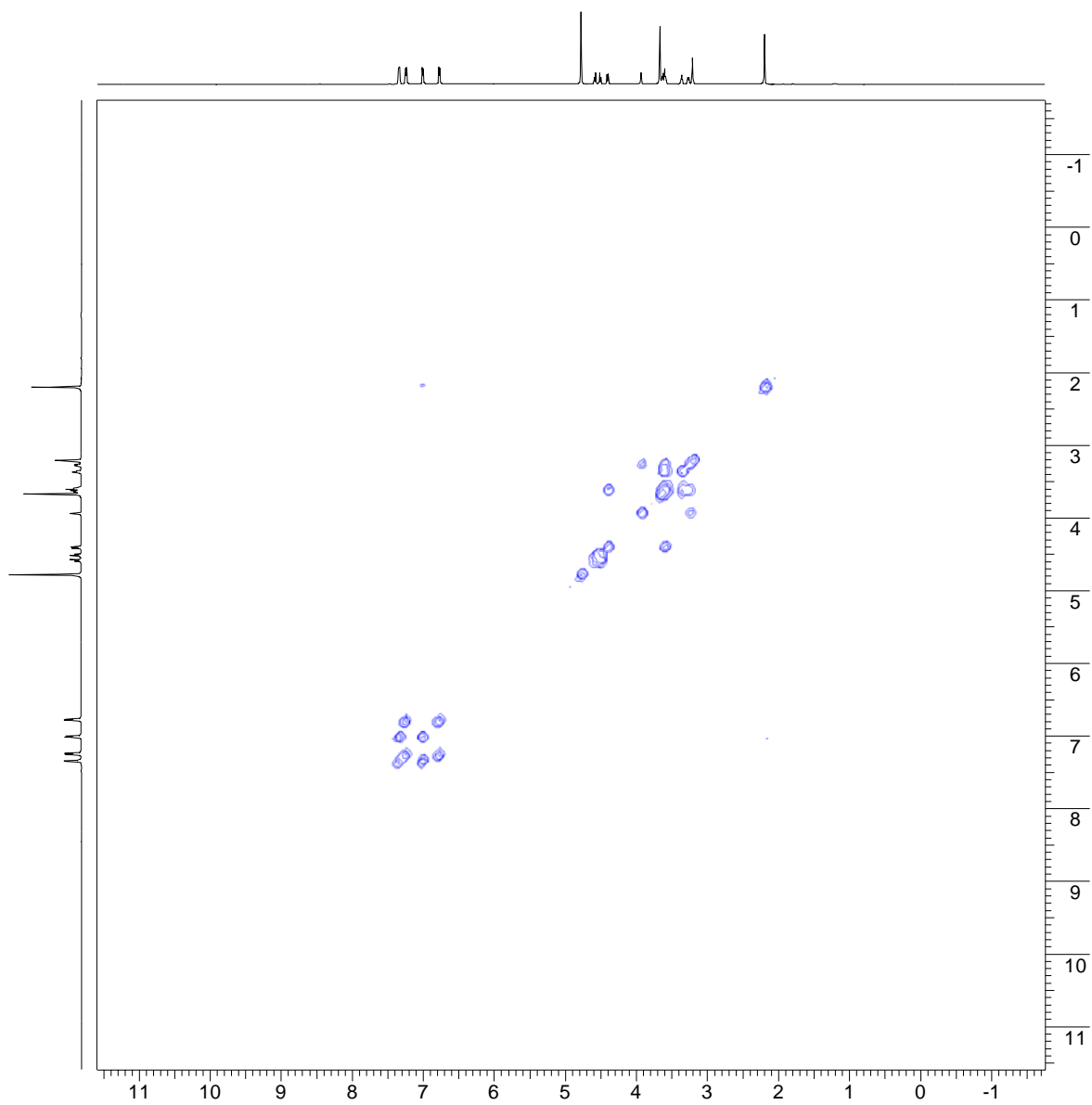
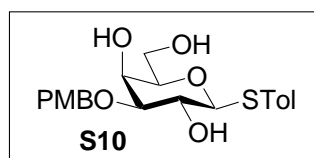
$^1\text{H-NMR}$  (600 MHz,  $\text{CD}_3\text{OD}$ )

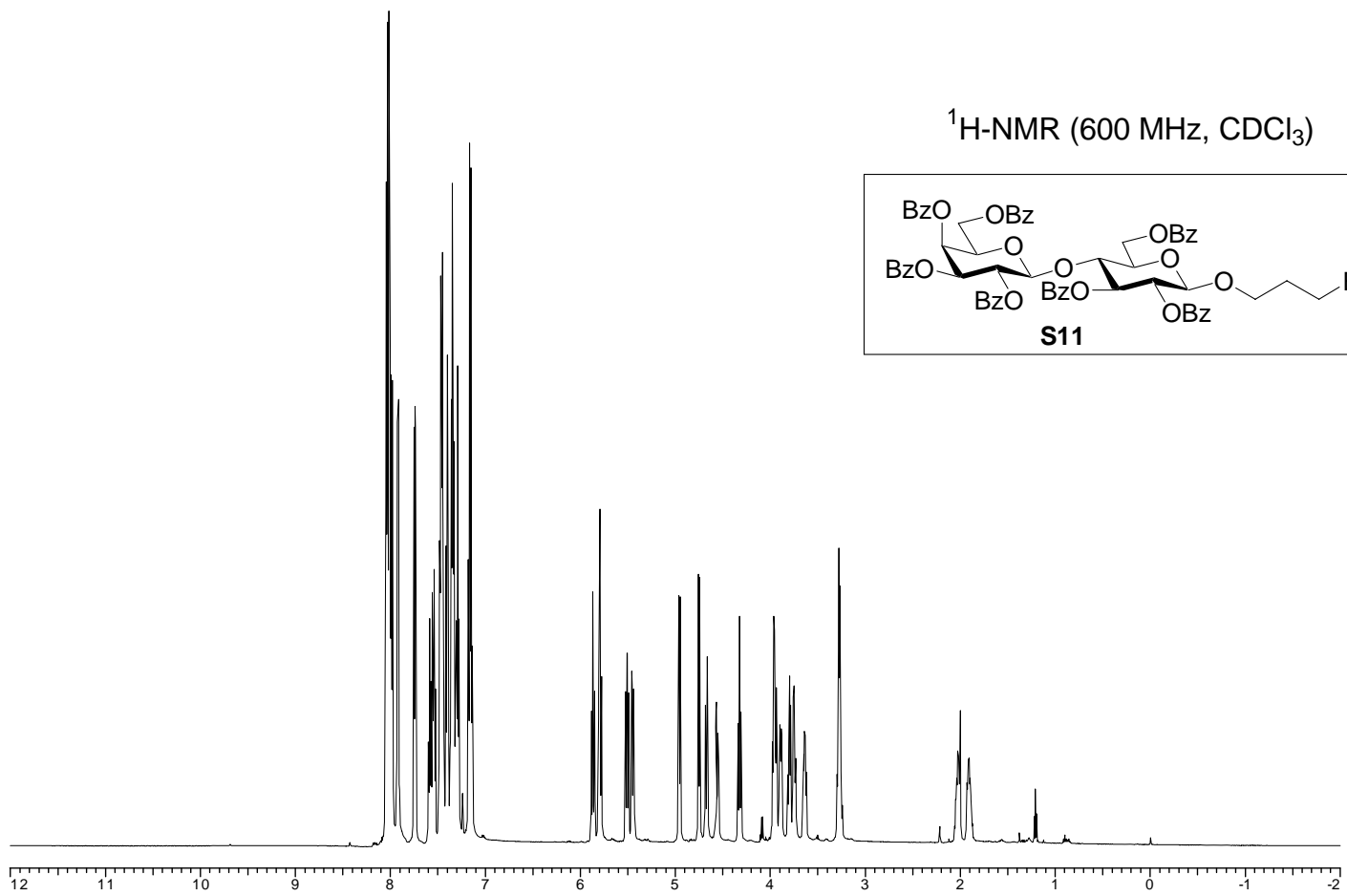


$^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_3\text{OD}$ )

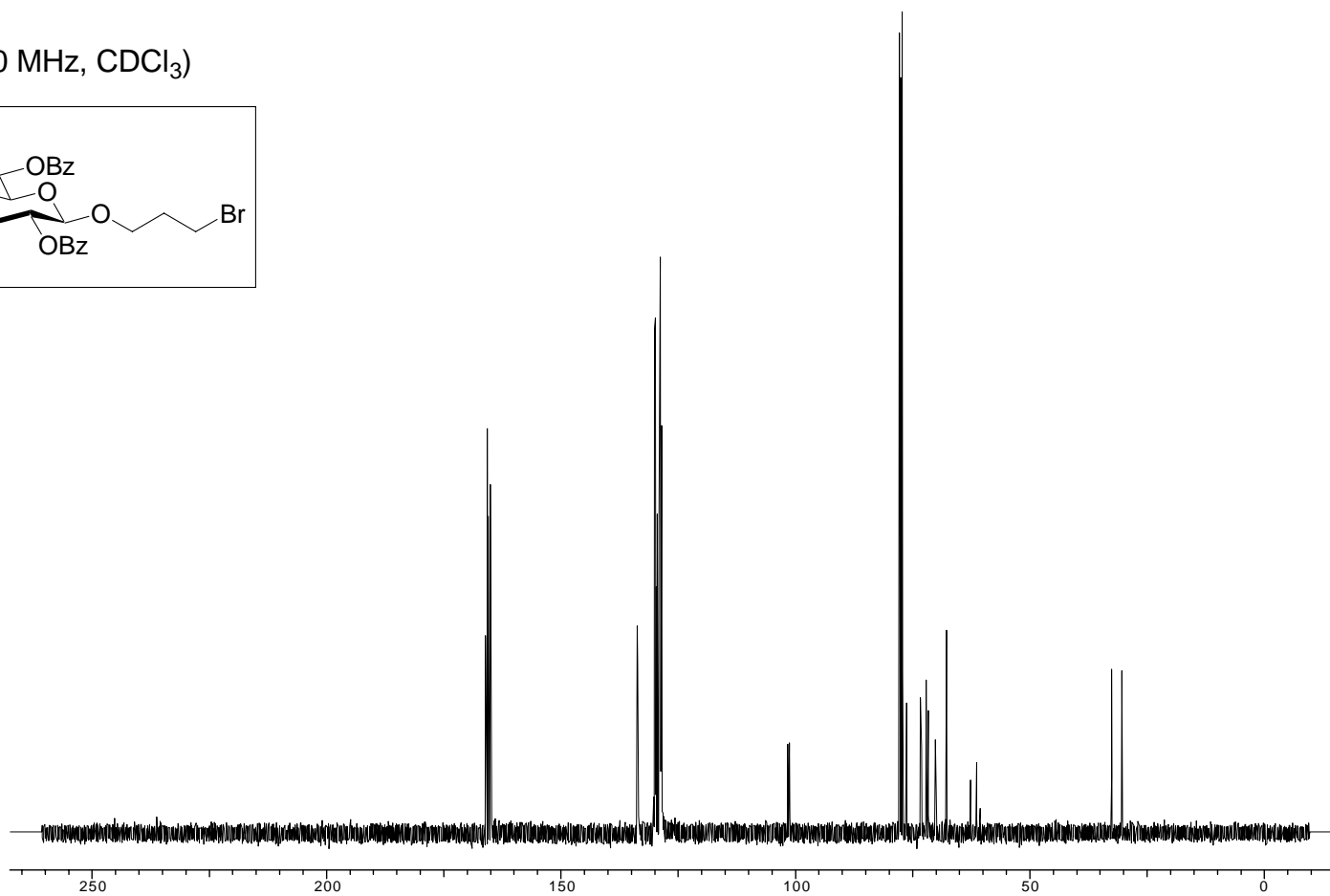
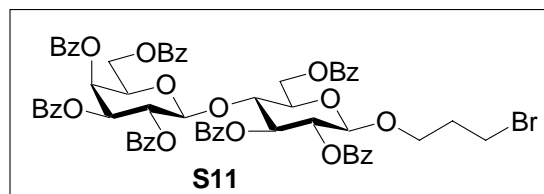


gCOSY (600 MHz, CD<sub>3</sub>OD)

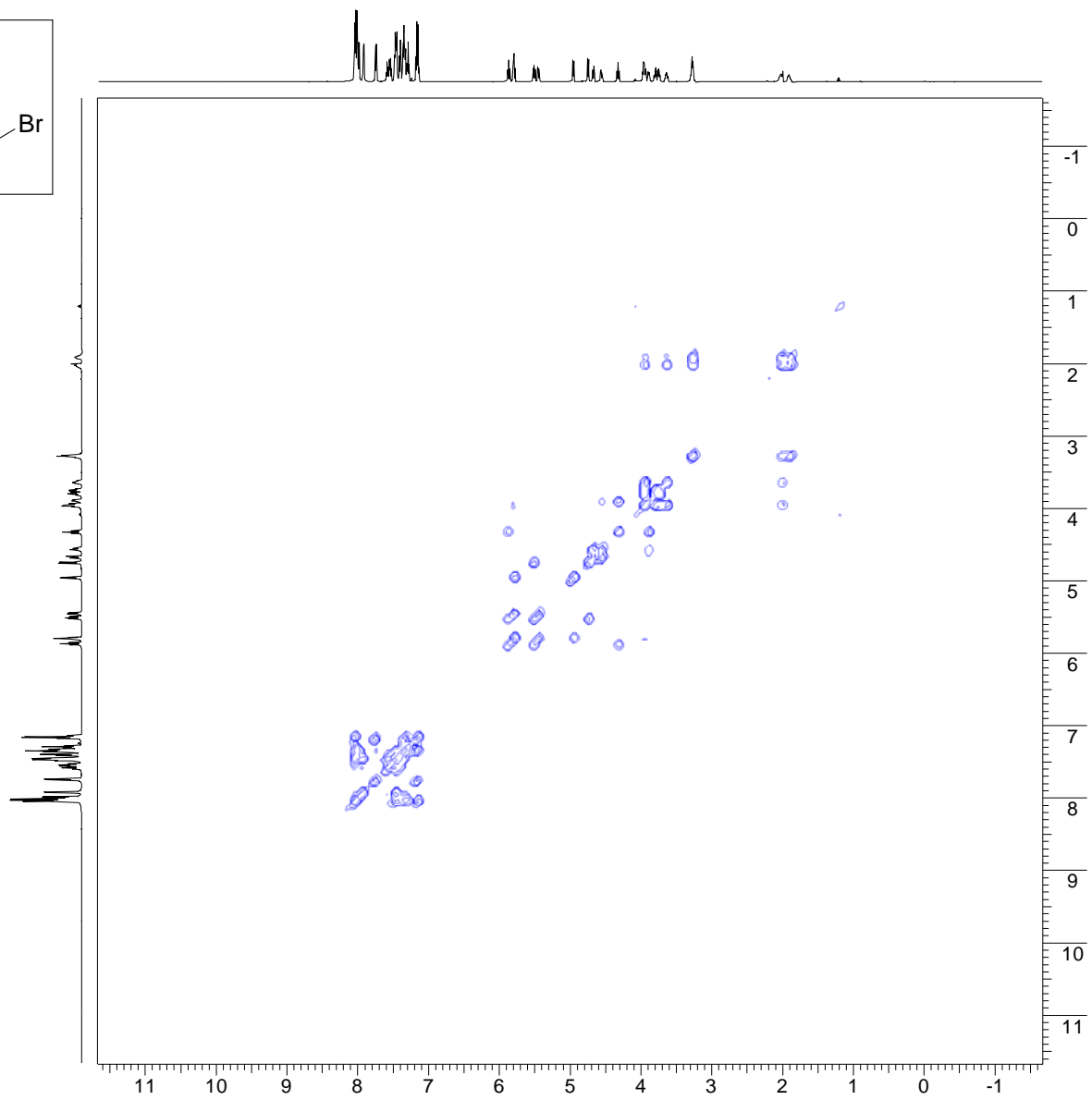
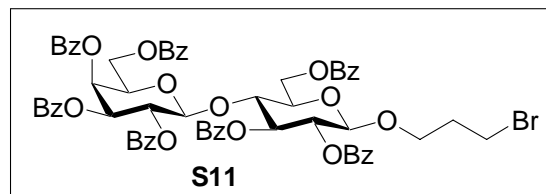




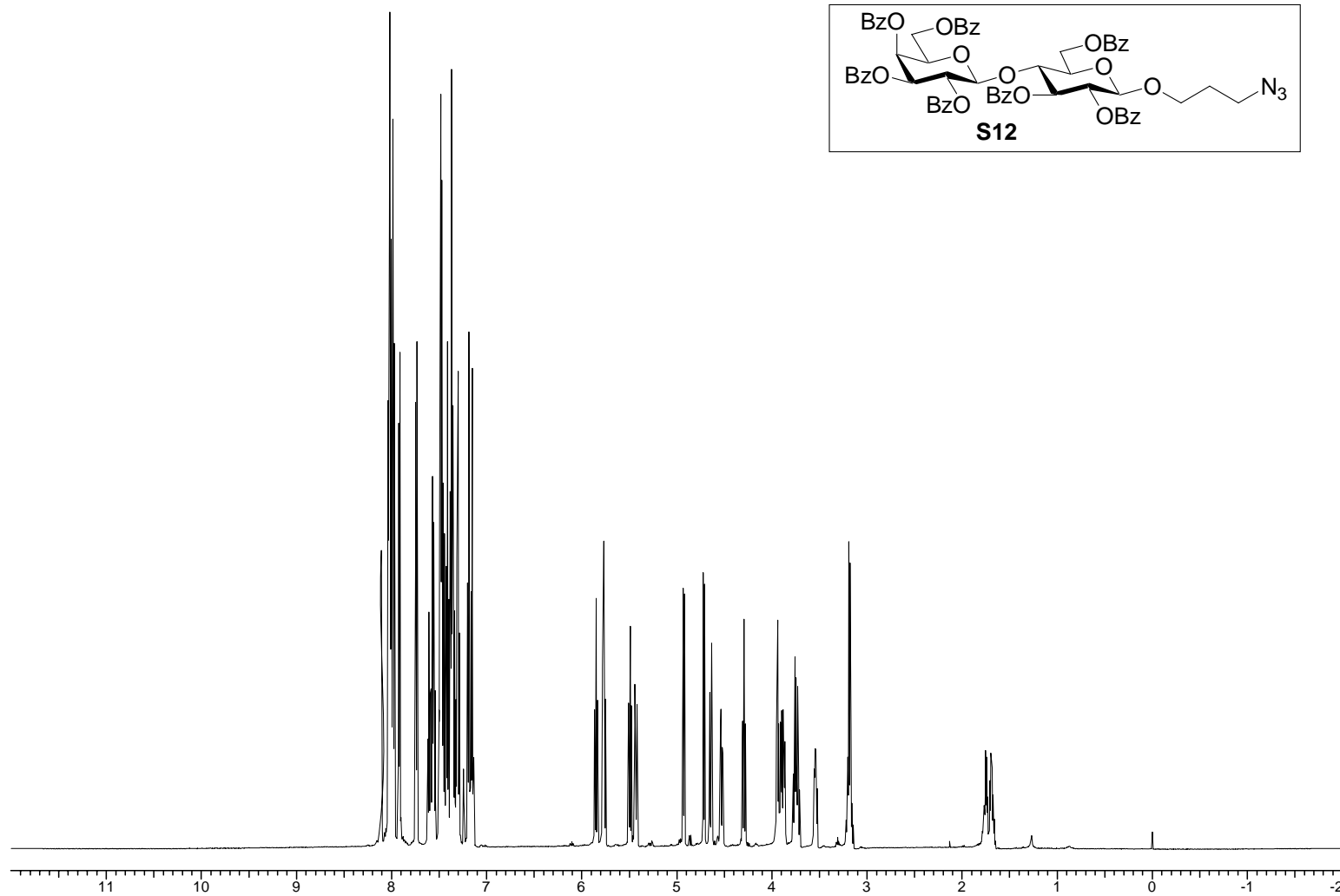
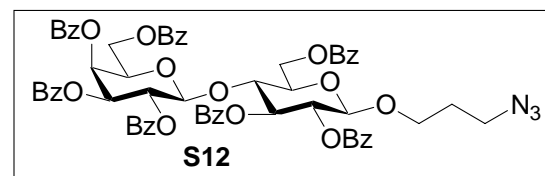
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )



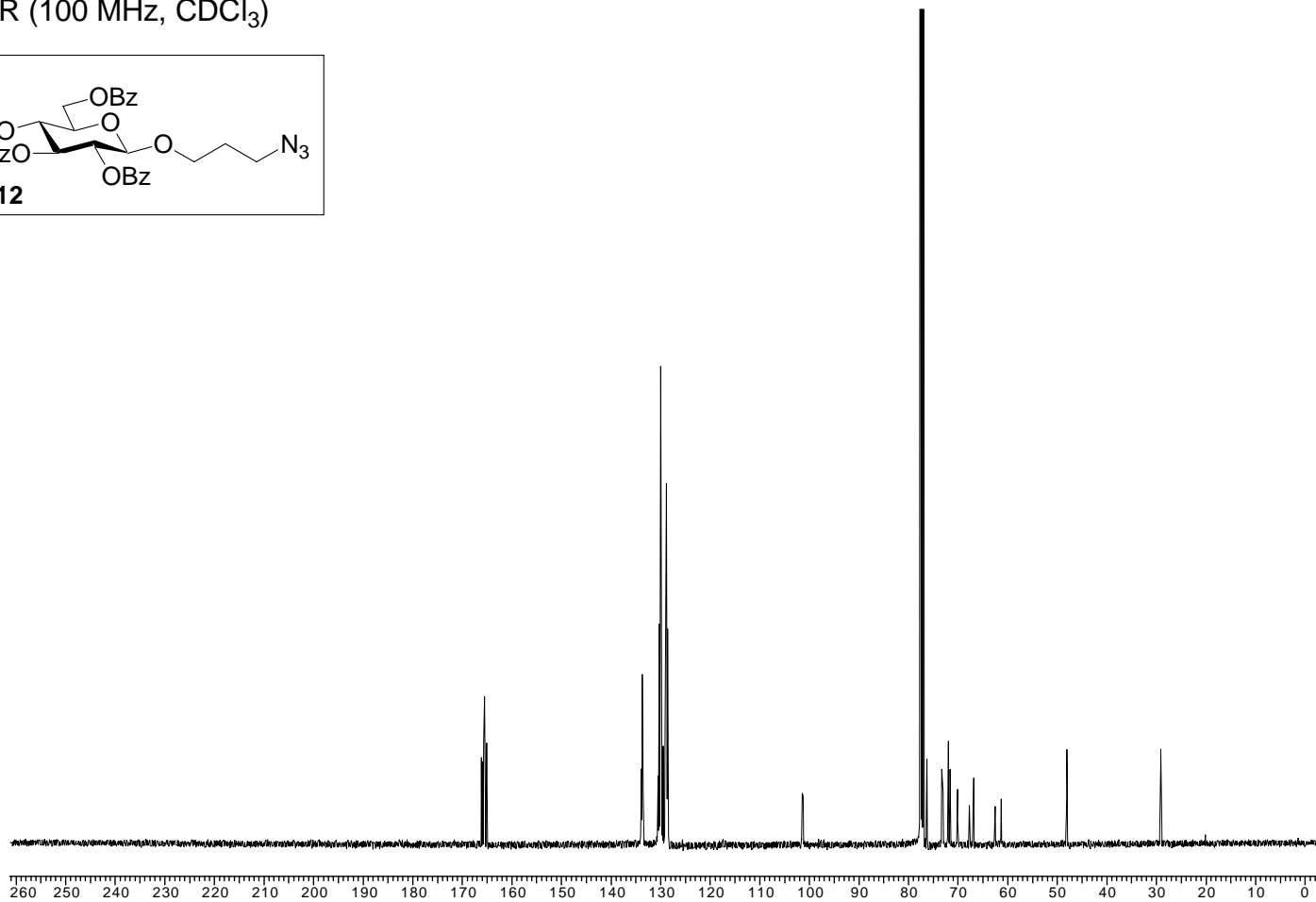
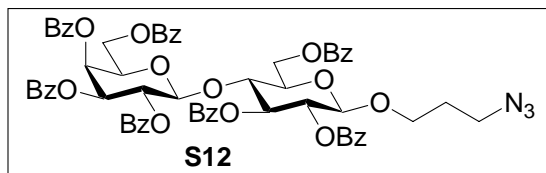
gCOSY (600 MHz, CDCl<sub>3</sub>)



$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

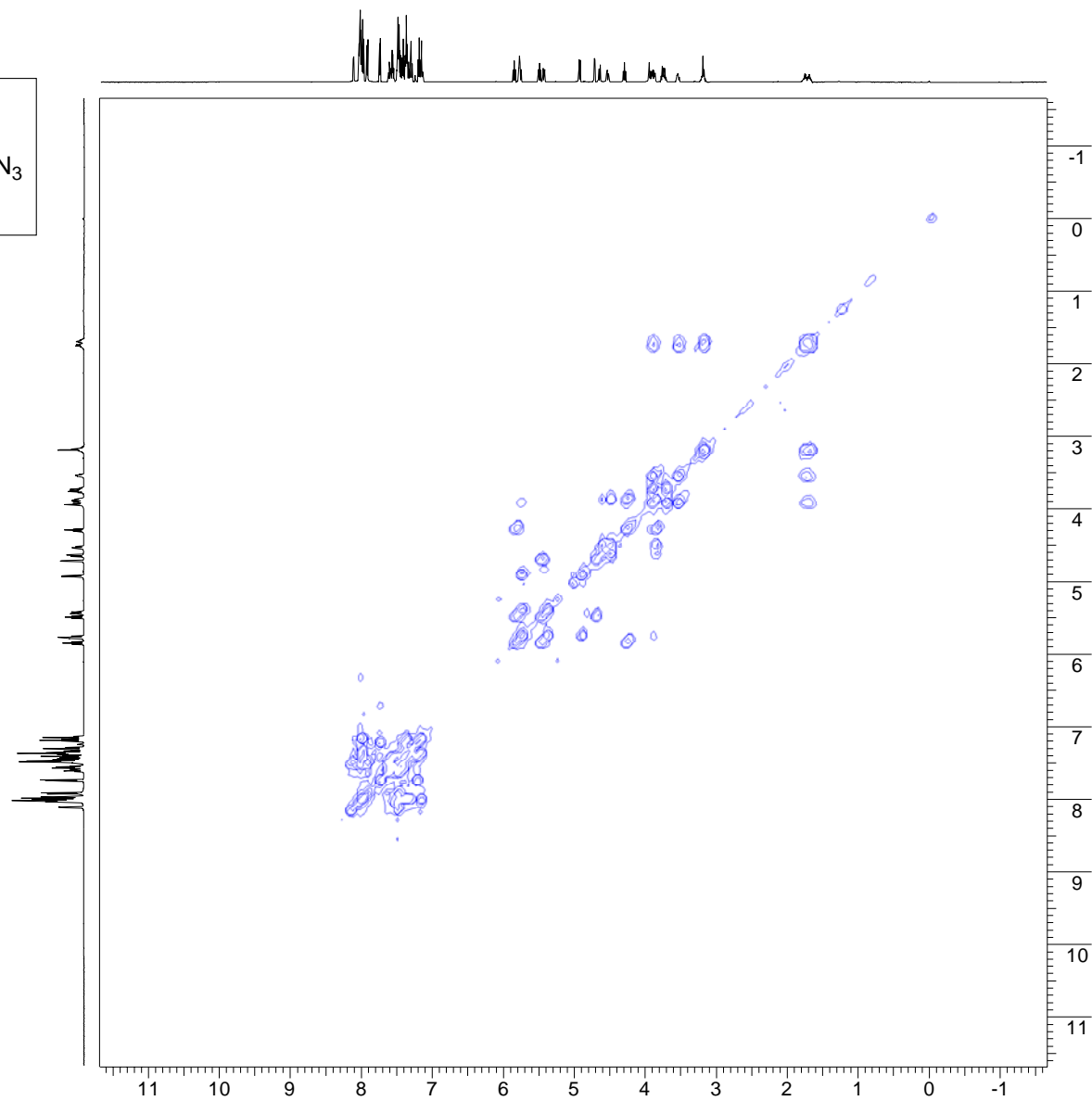
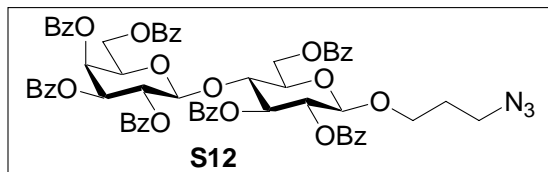


$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )

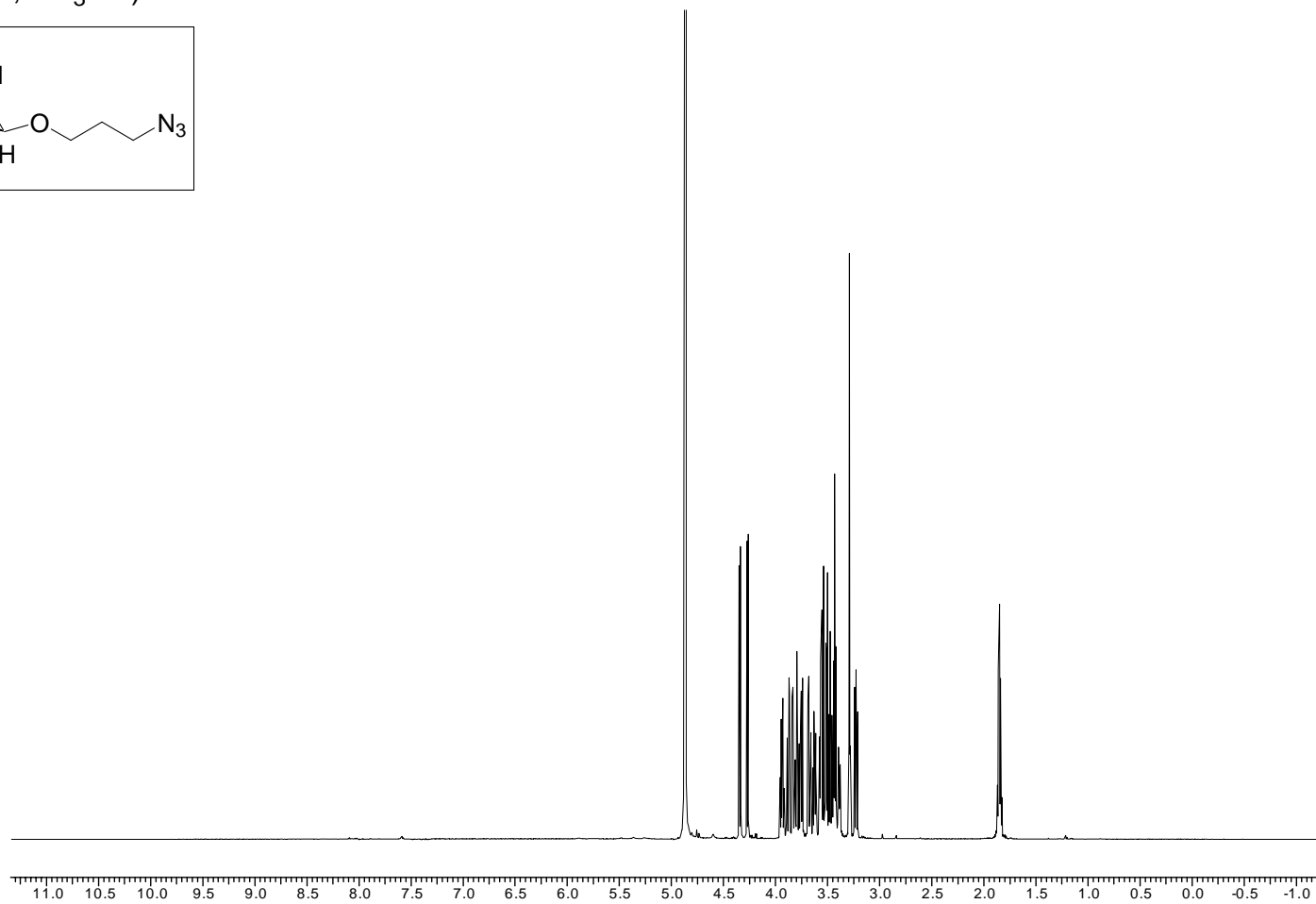
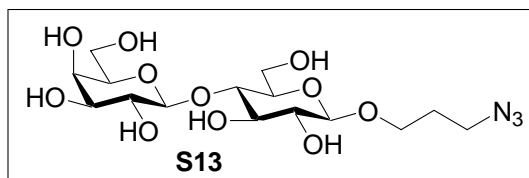




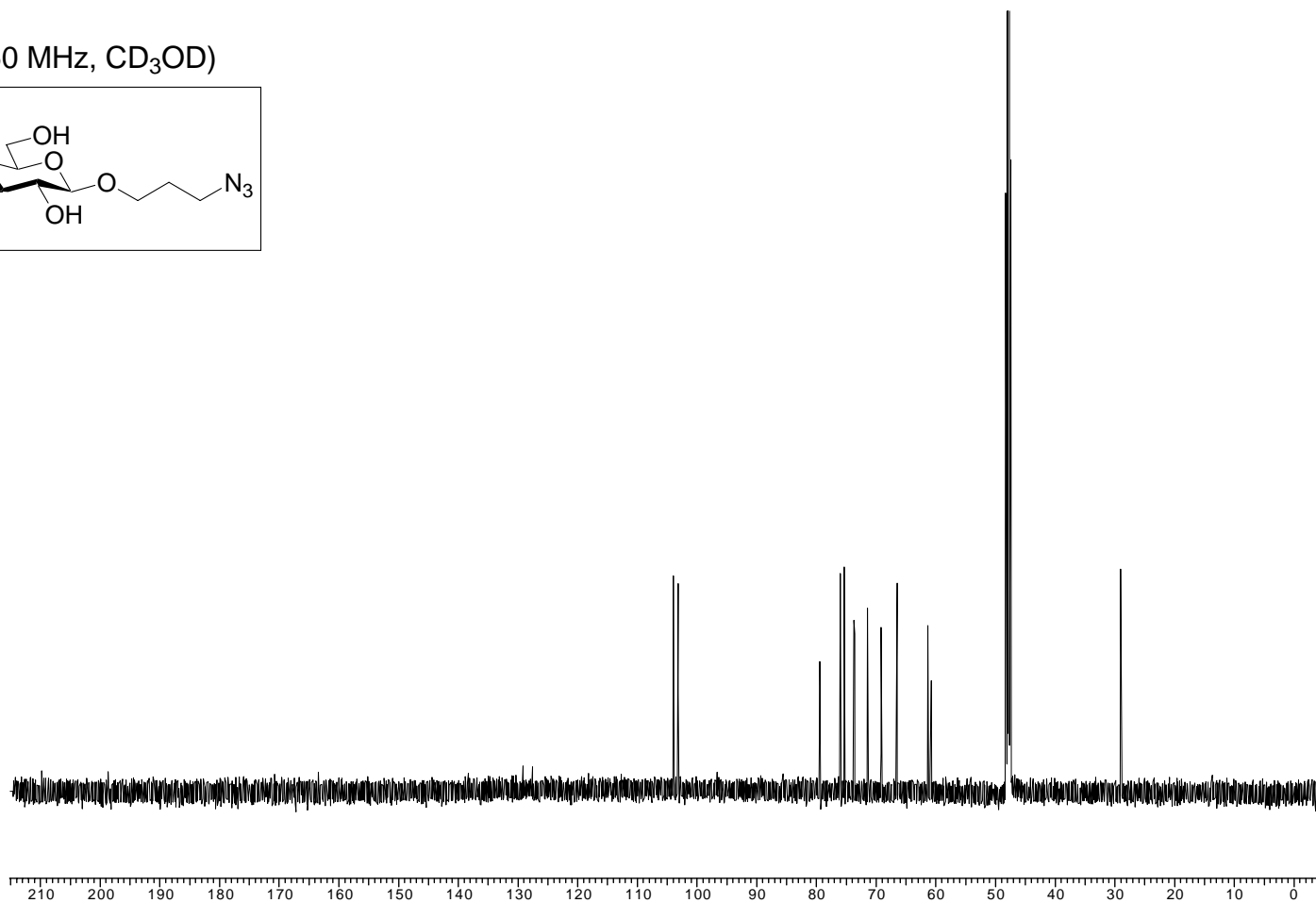
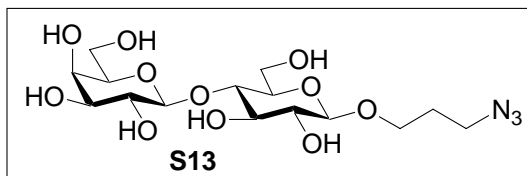
gCOSY (600 MHz, CDCl<sub>3</sub>)



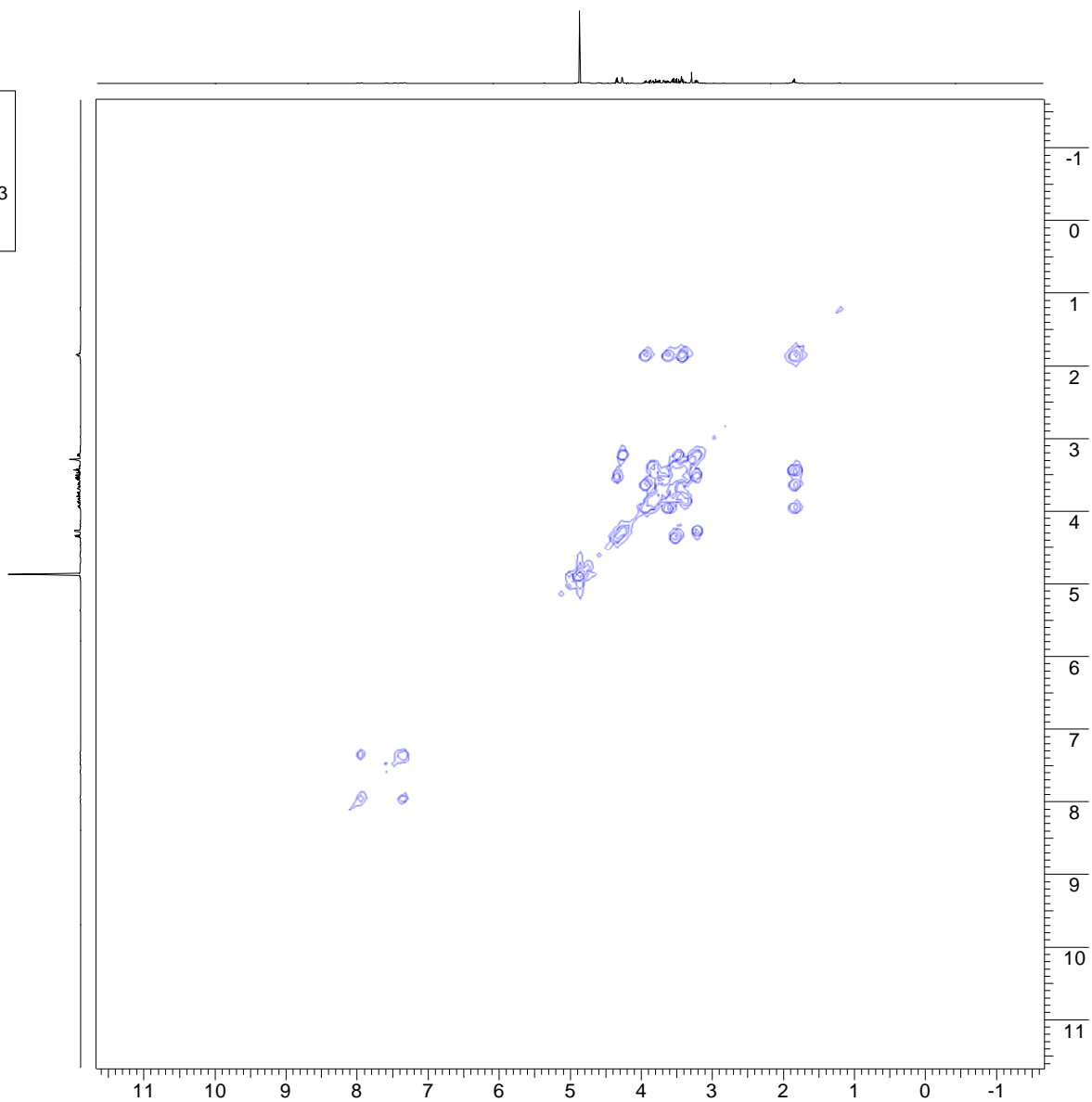
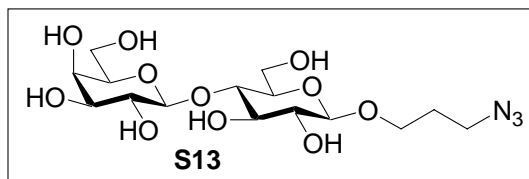
$^1\text{H-NMR}$  (600 MHz,  $\text{CD}_3\text{OD}$ )



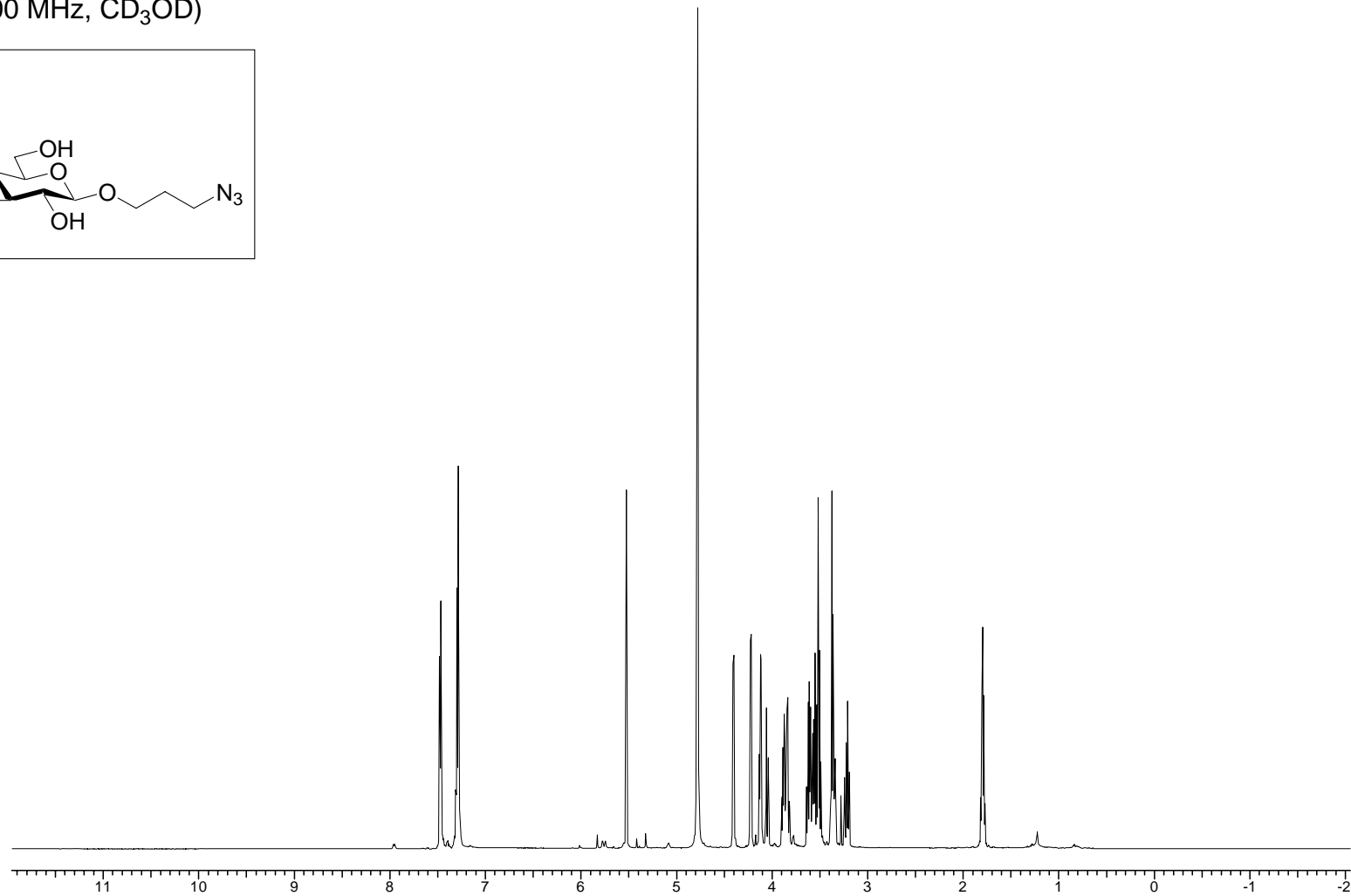
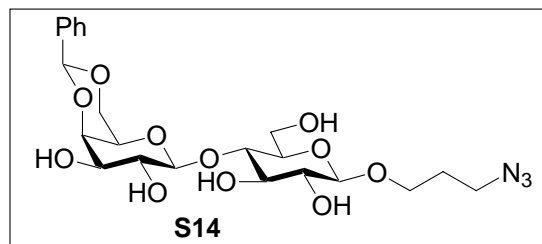
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CD}_3\text{OD}$ )



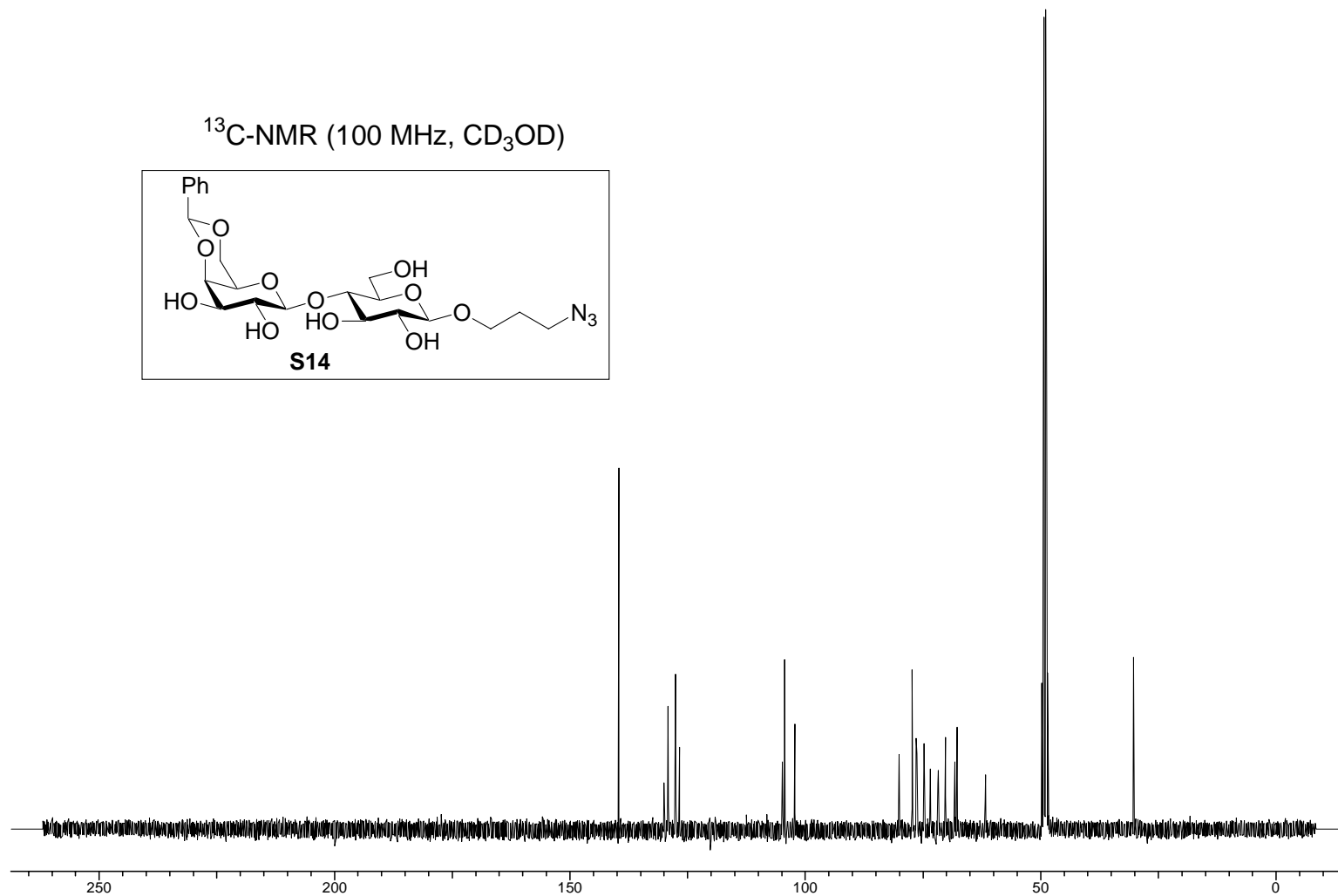
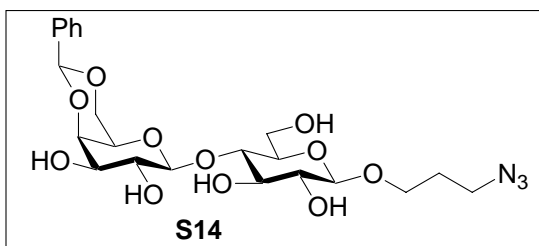
gCOSY (600 MHz, CD<sub>3</sub>OD)



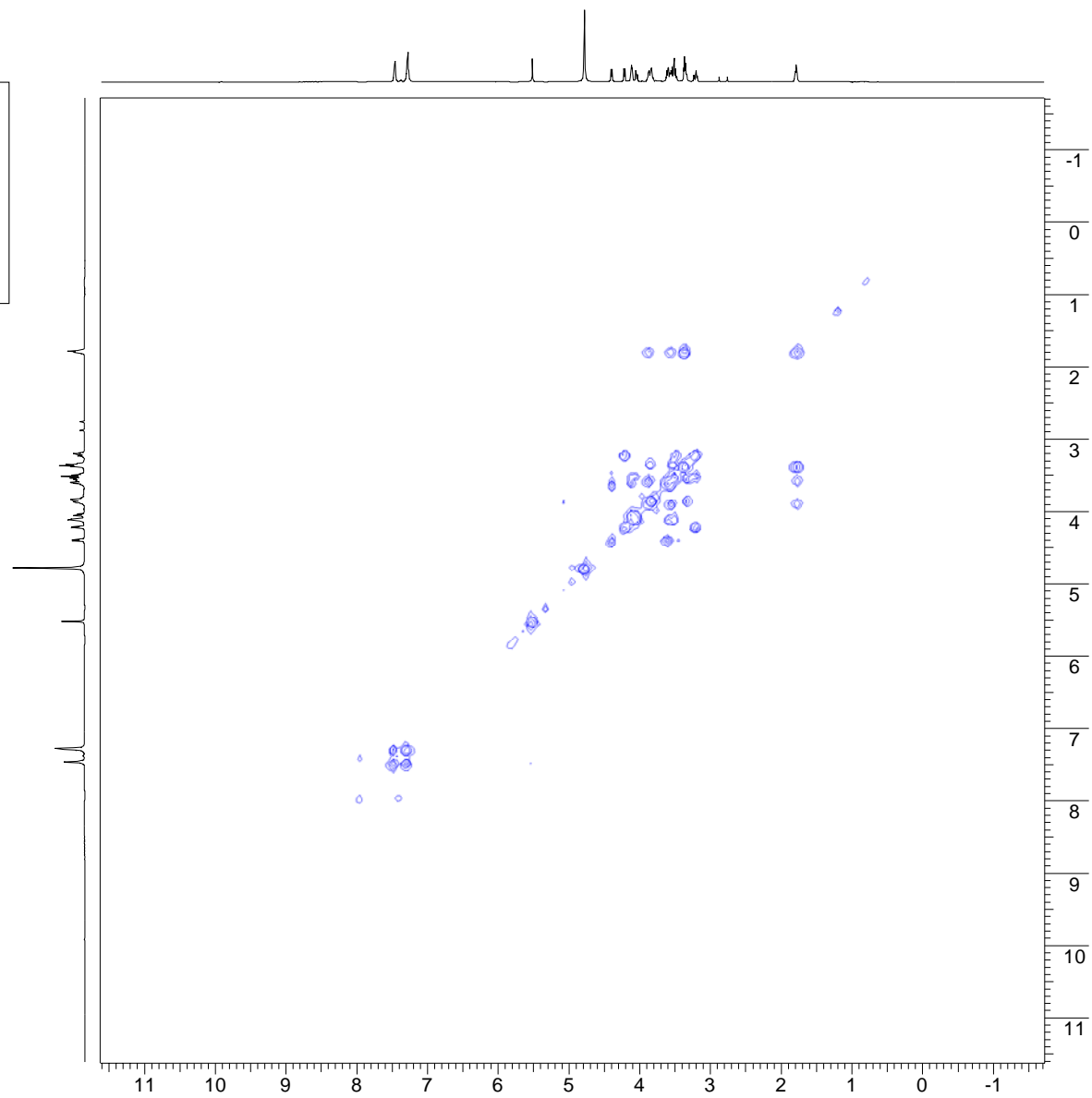
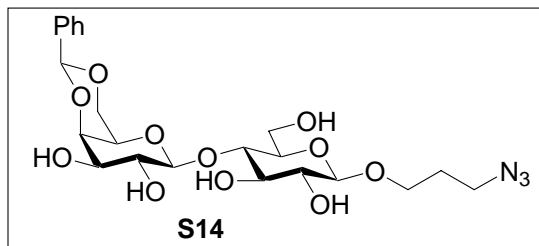
$^1\text{H-NMR}$  (600 MHz,  $\text{CD}_3\text{OD}$ )



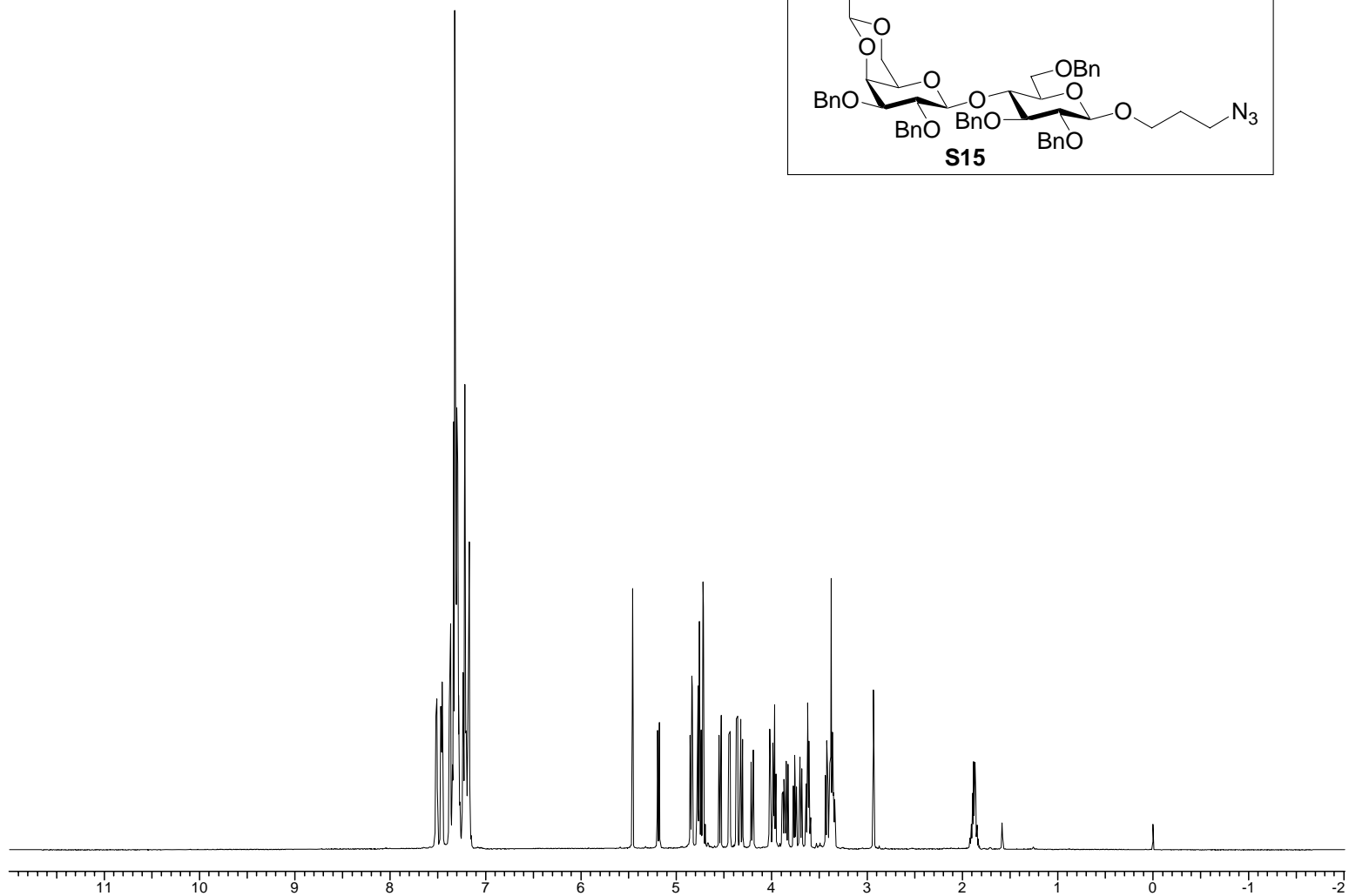
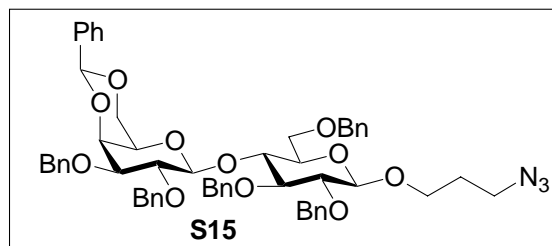
$^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_3\text{OD}$ )



gCOSY (600 MHz, CD<sub>3</sub>OD)

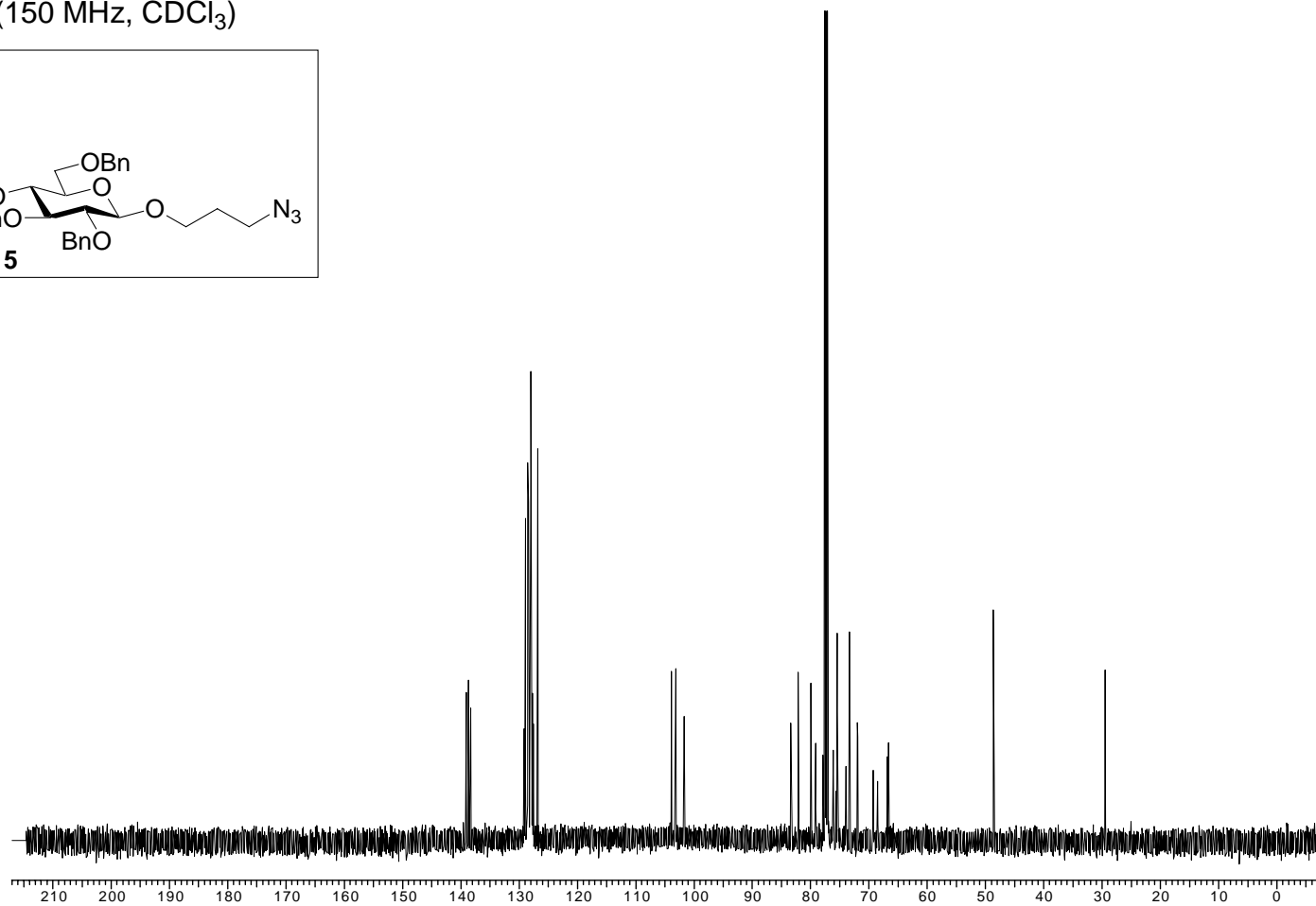
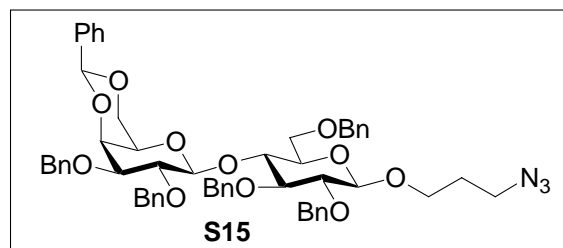


$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )

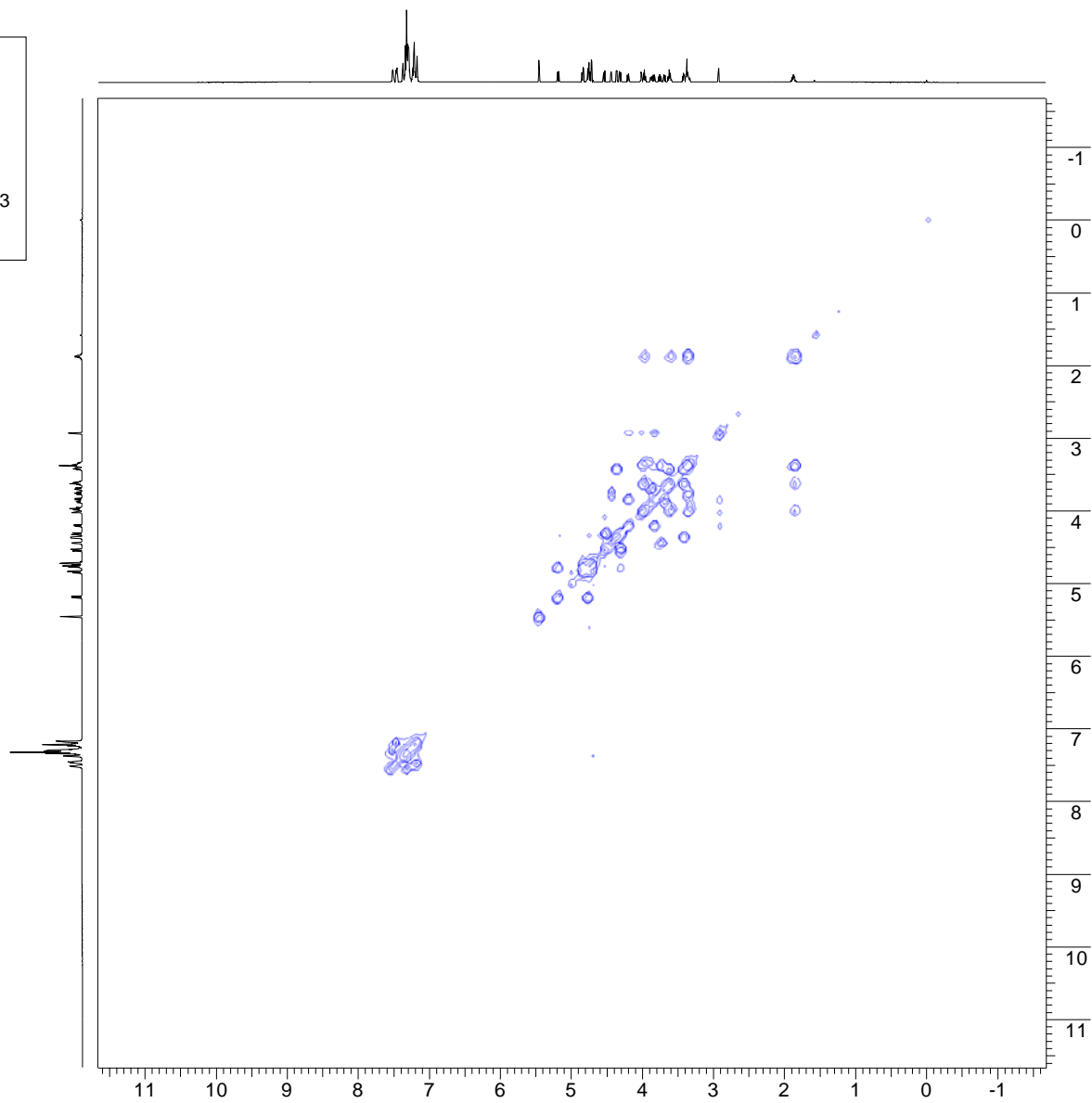
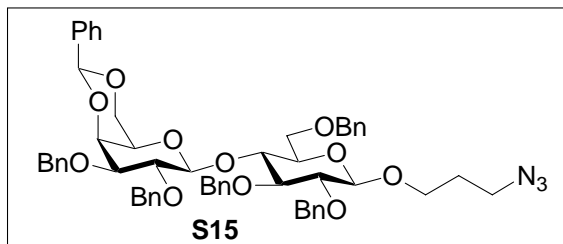




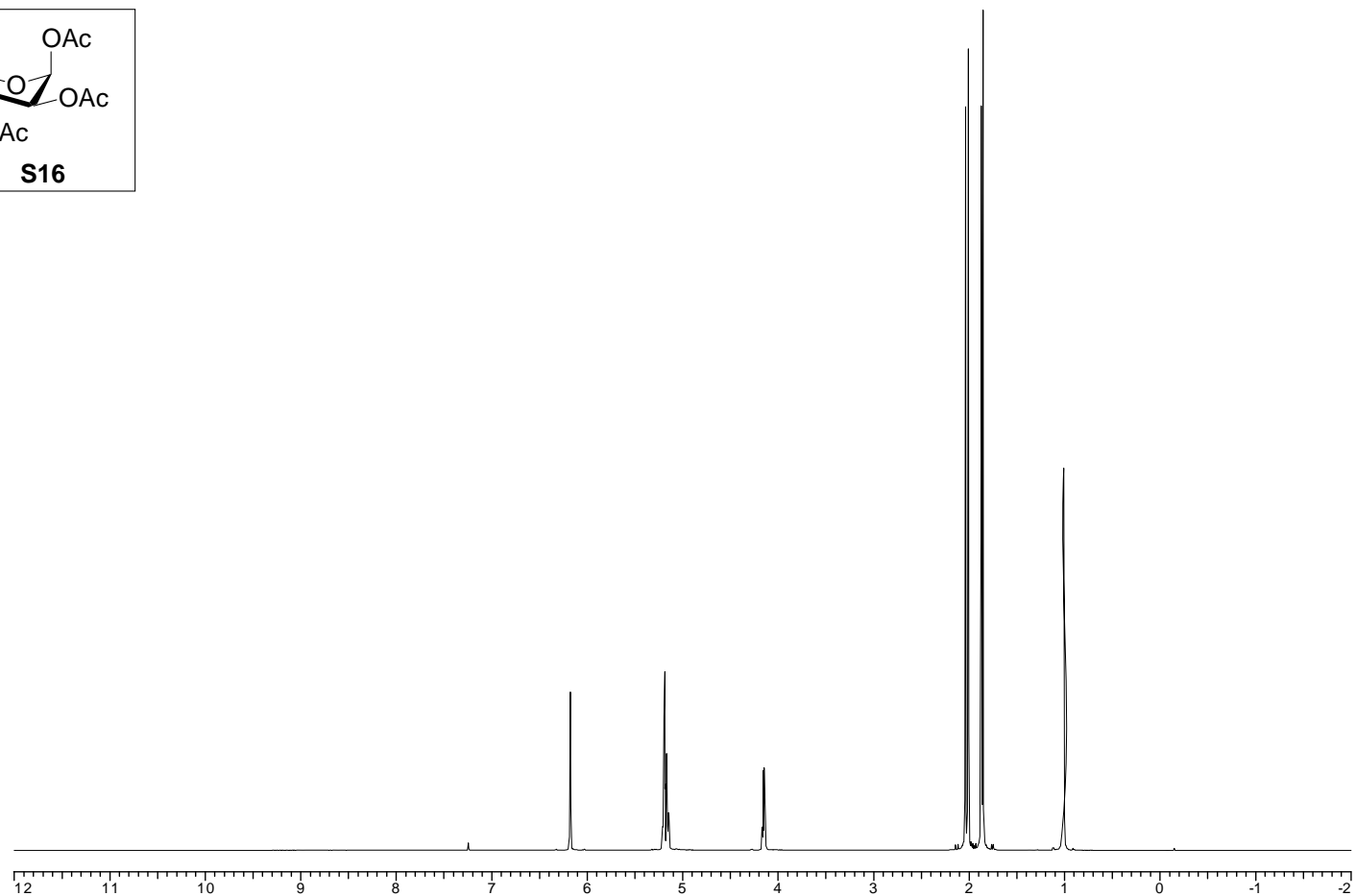
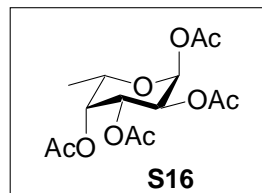
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



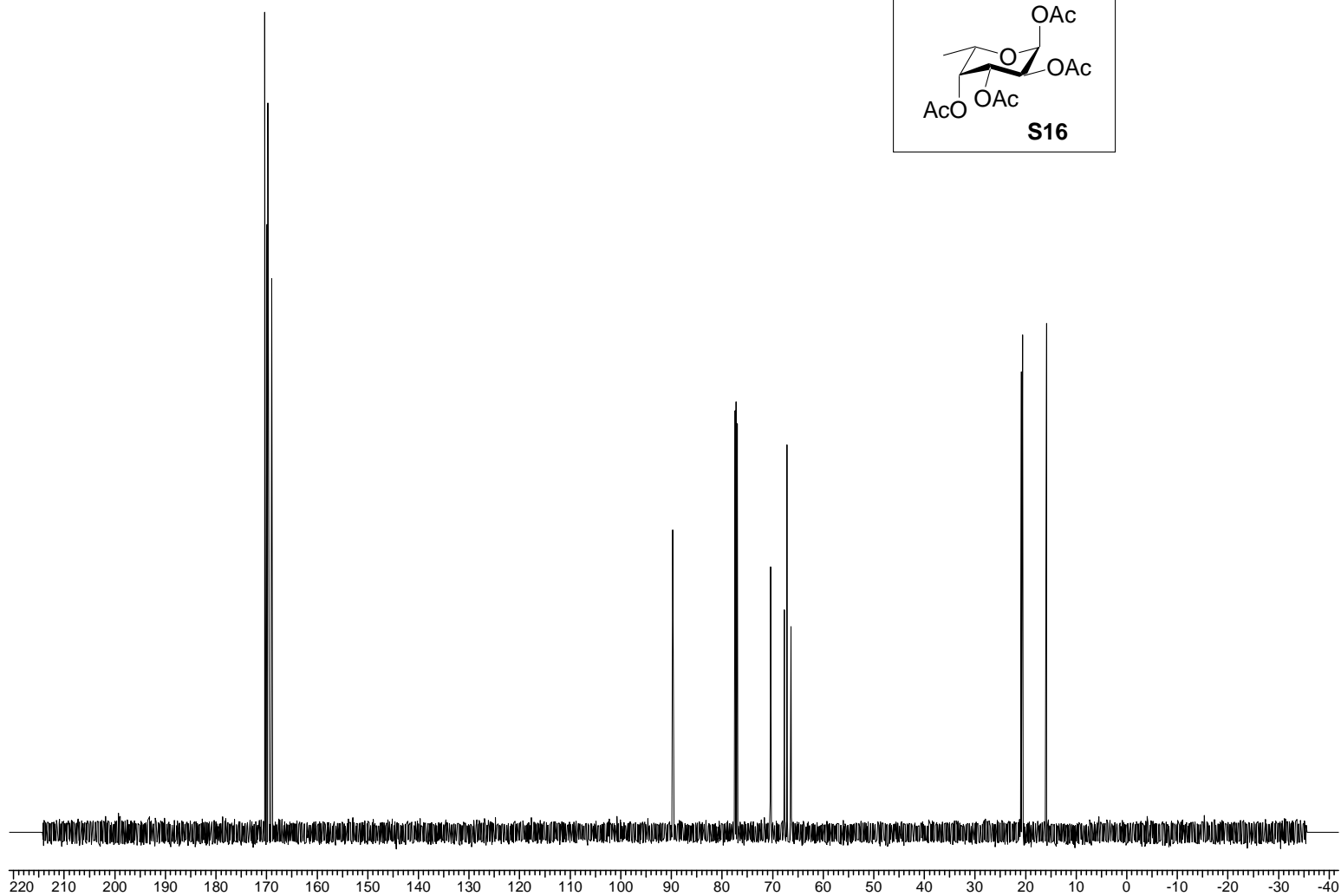
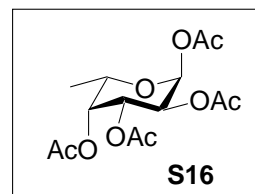
gCOSY (600 MHz, CDCl<sub>3</sub>)



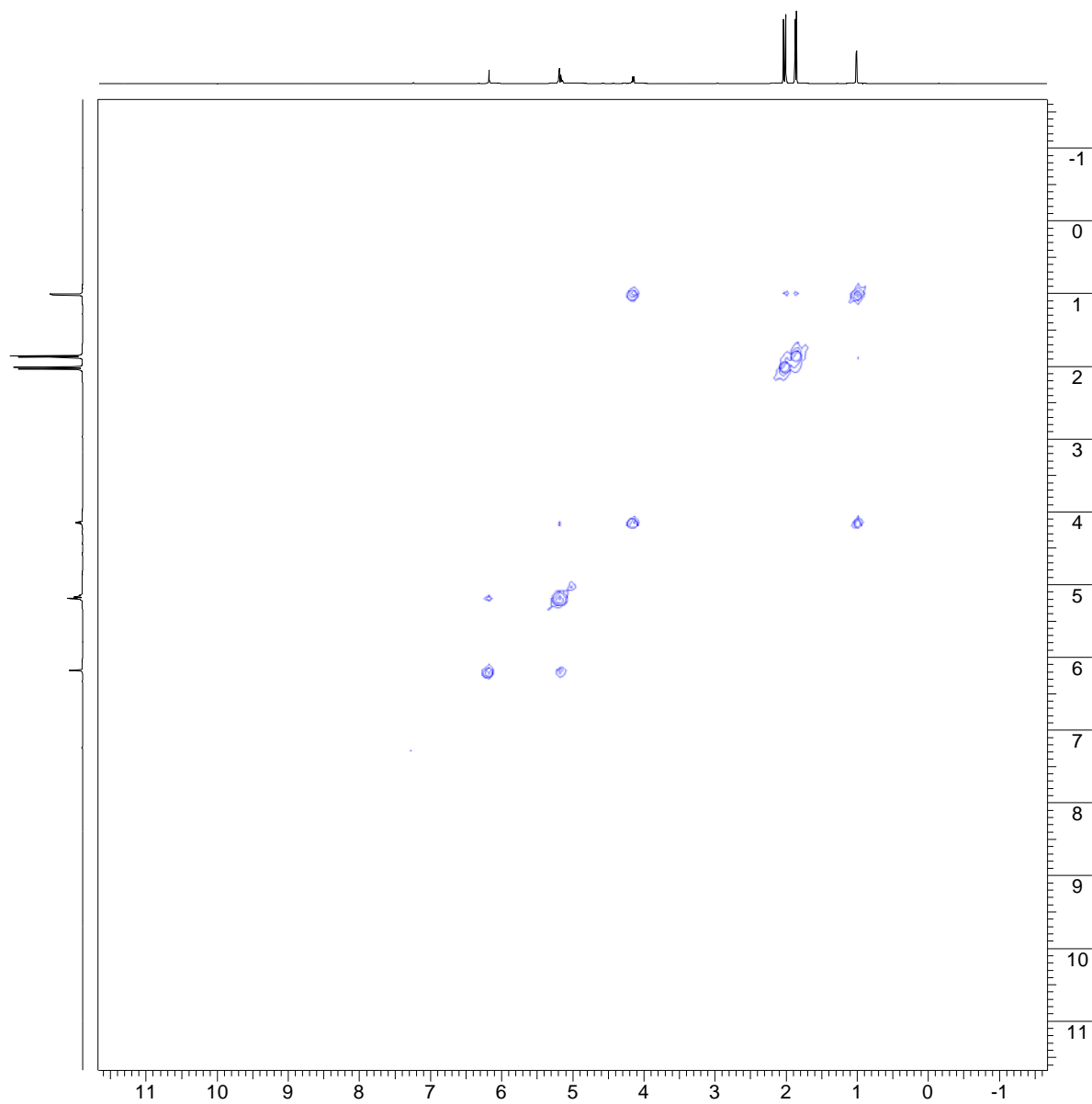
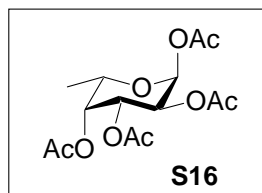
$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



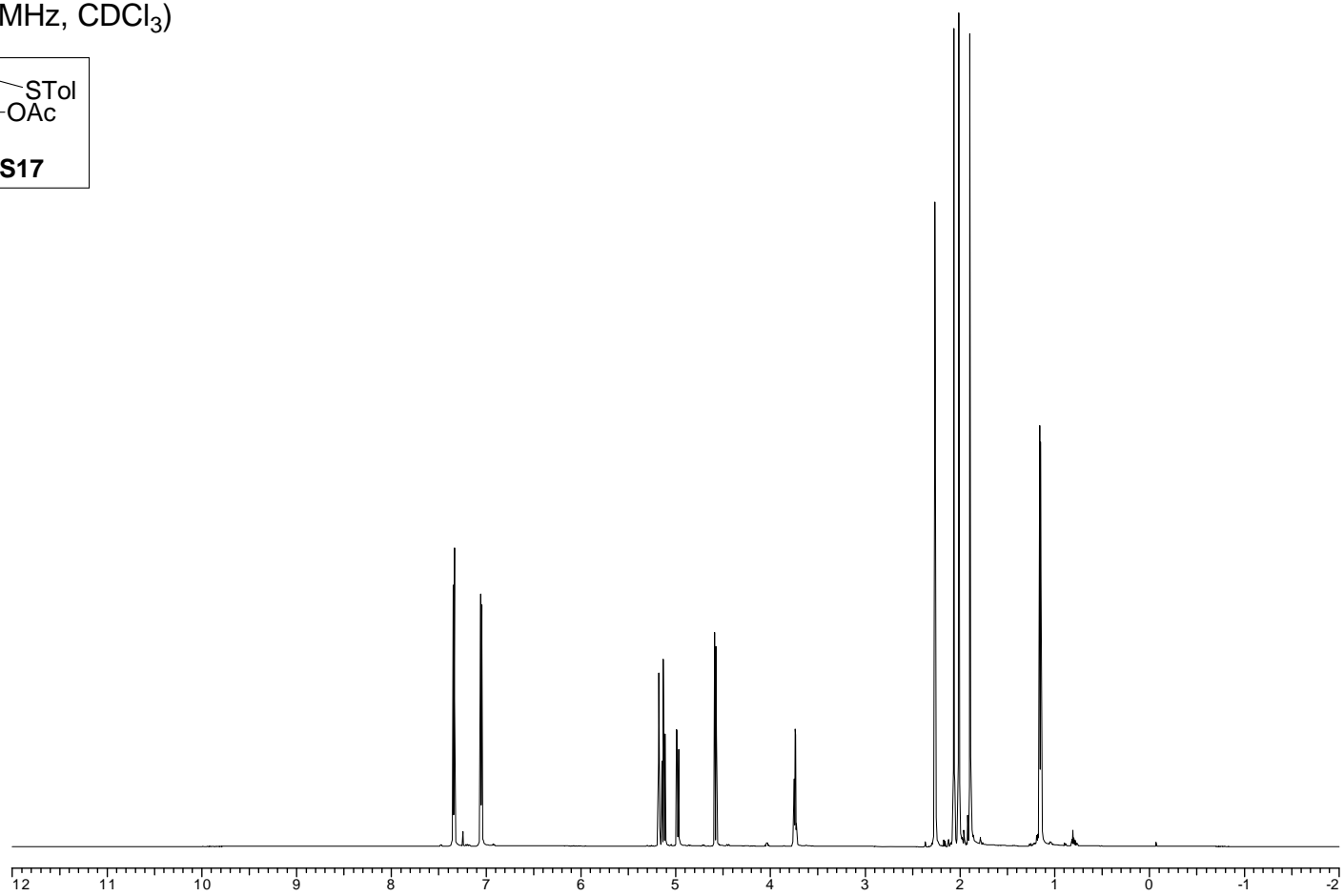
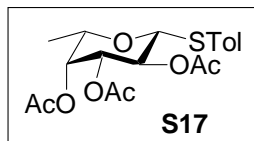
$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



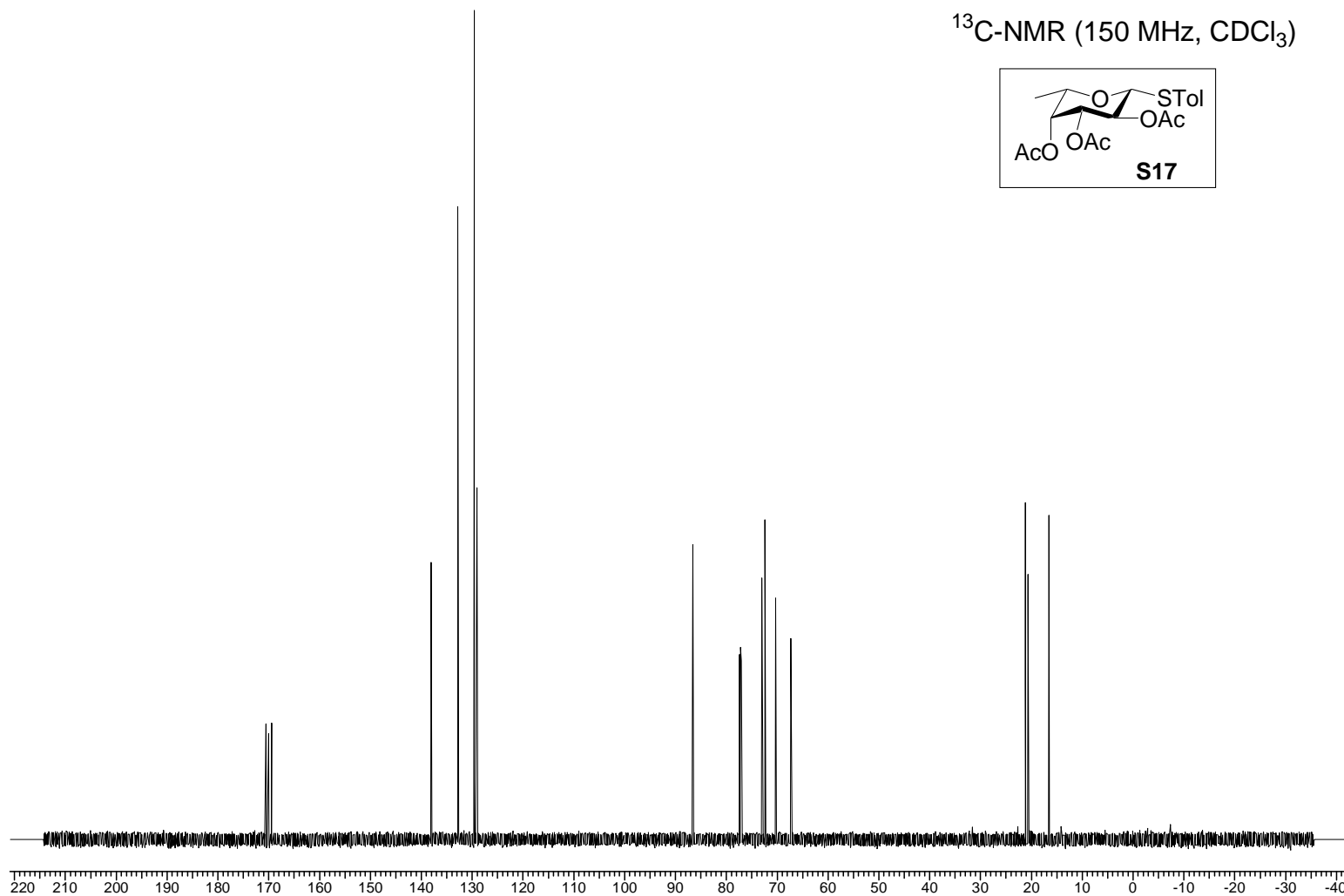
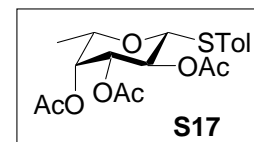
gCOSY (600 MHz, CDCl<sub>3</sub>)



$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$ -NMR (150 MHz,  $\text{CDCl}_3$ )



gCOSY (600 MHz, CDCl<sub>3</sub>)

