

## Supporting Information File 2

for

### Synthesis of glycoconjugate fragments of mycobacterial phosphatidylinositol mannosides and lipomannan

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**<sup>1</sup>H and <sup>13</sup>C NMR spectra for new compounds and fluorescence spectra for 5–7**

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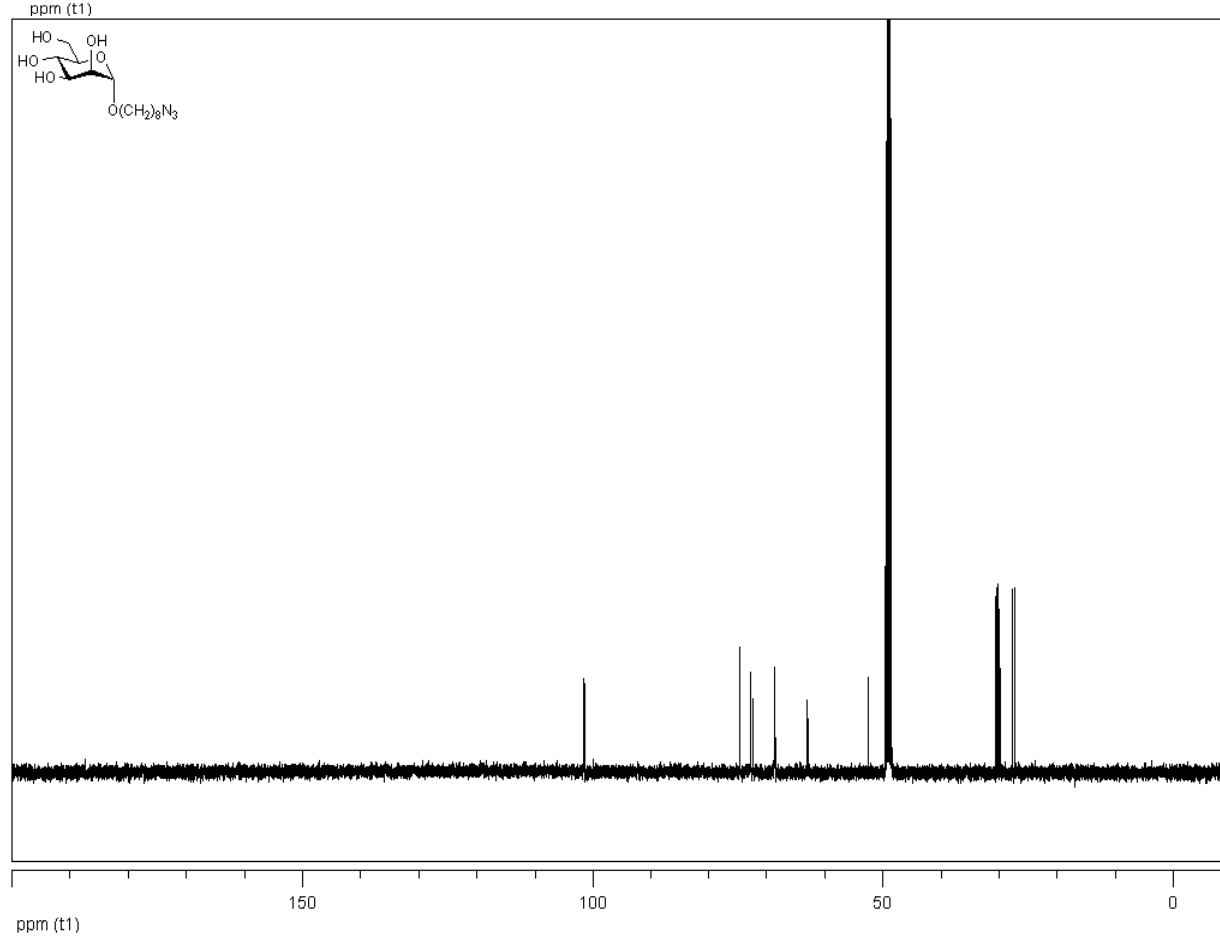
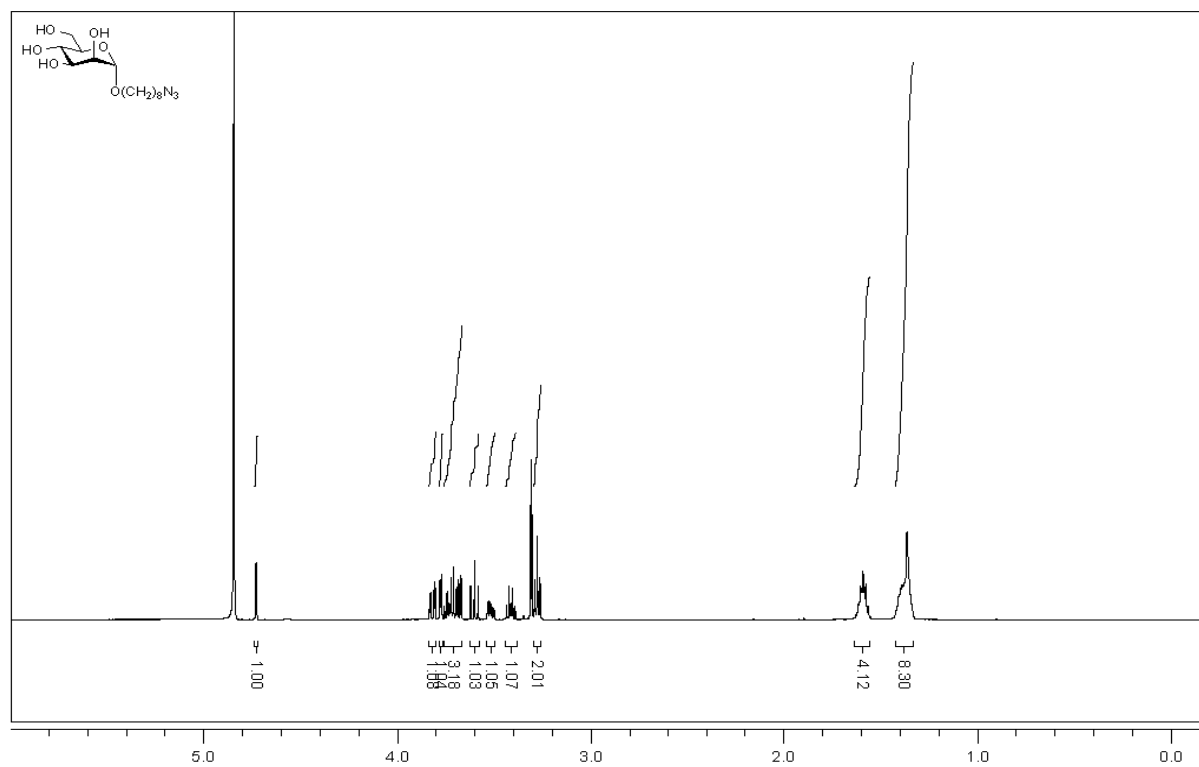
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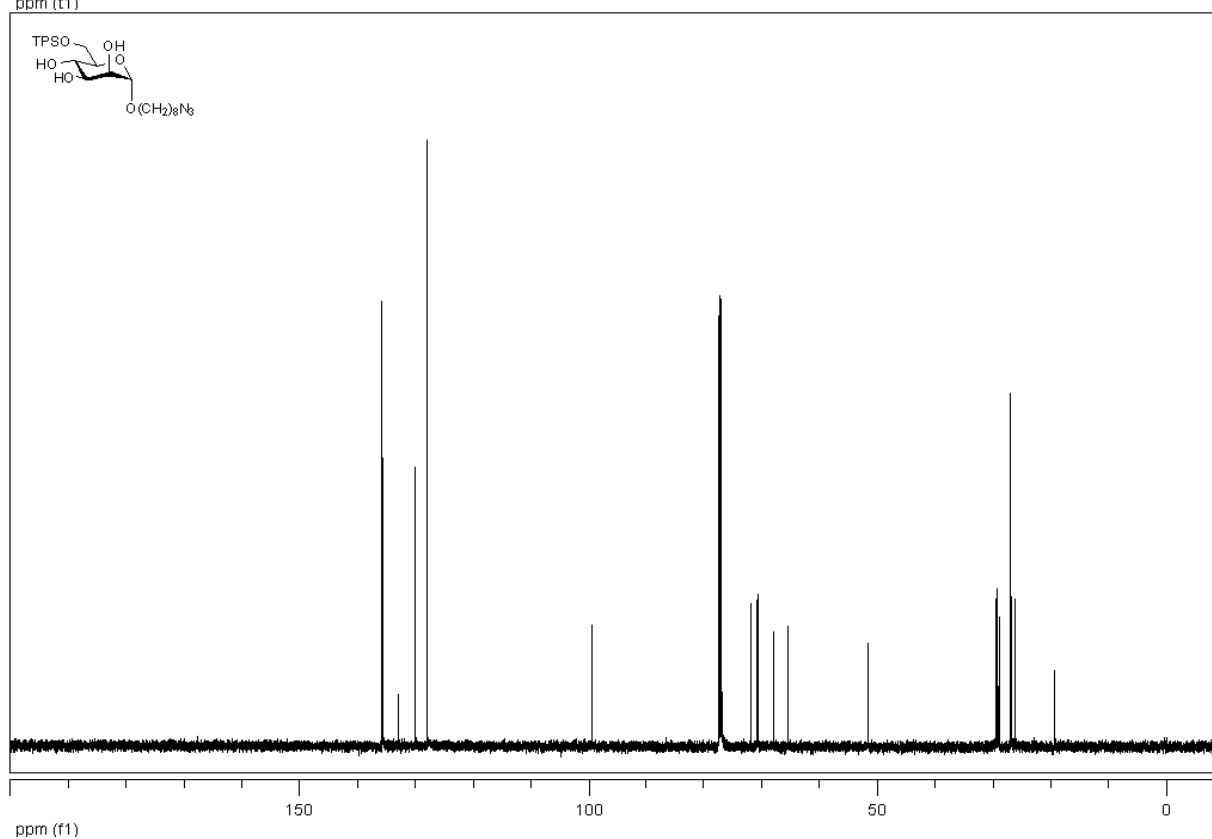
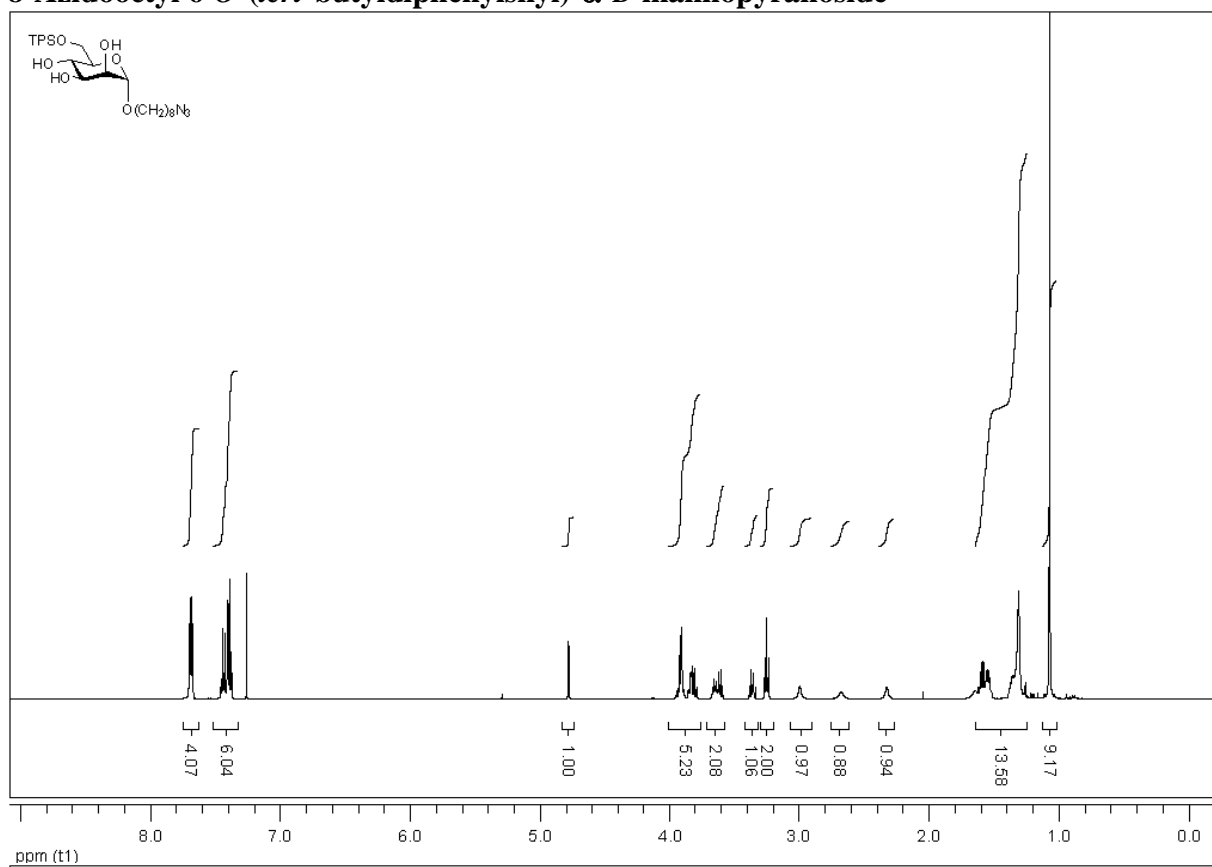
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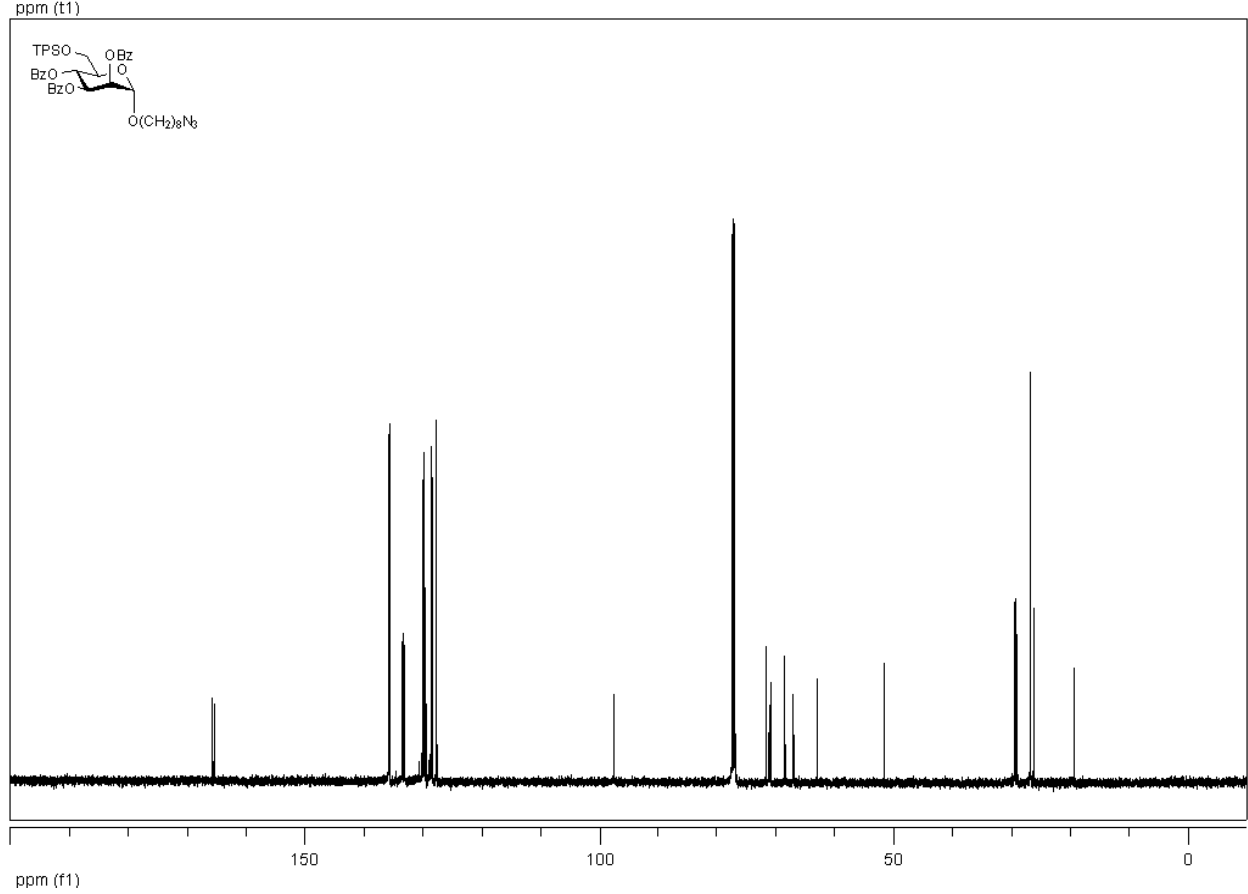
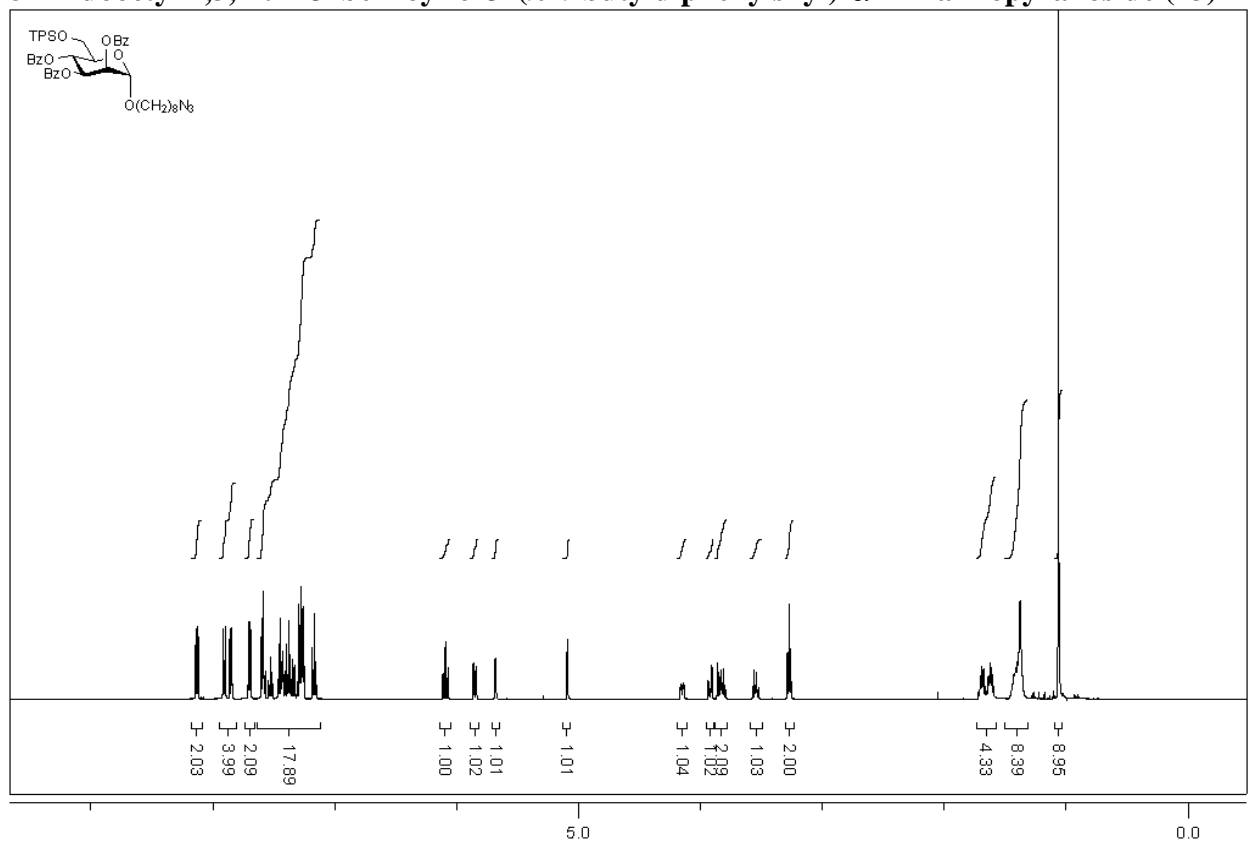
# Azidoethyl $\alpha$ -D-mannopyranoside (12)



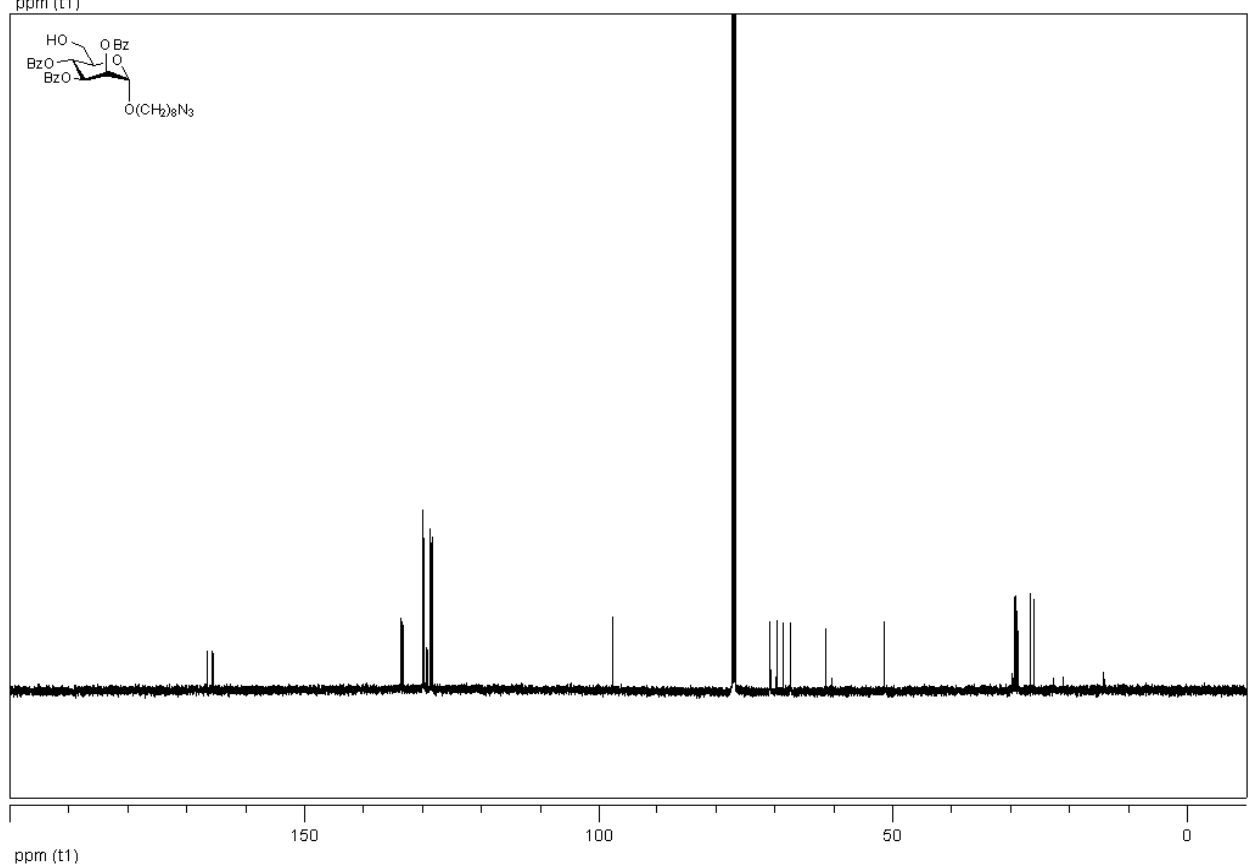
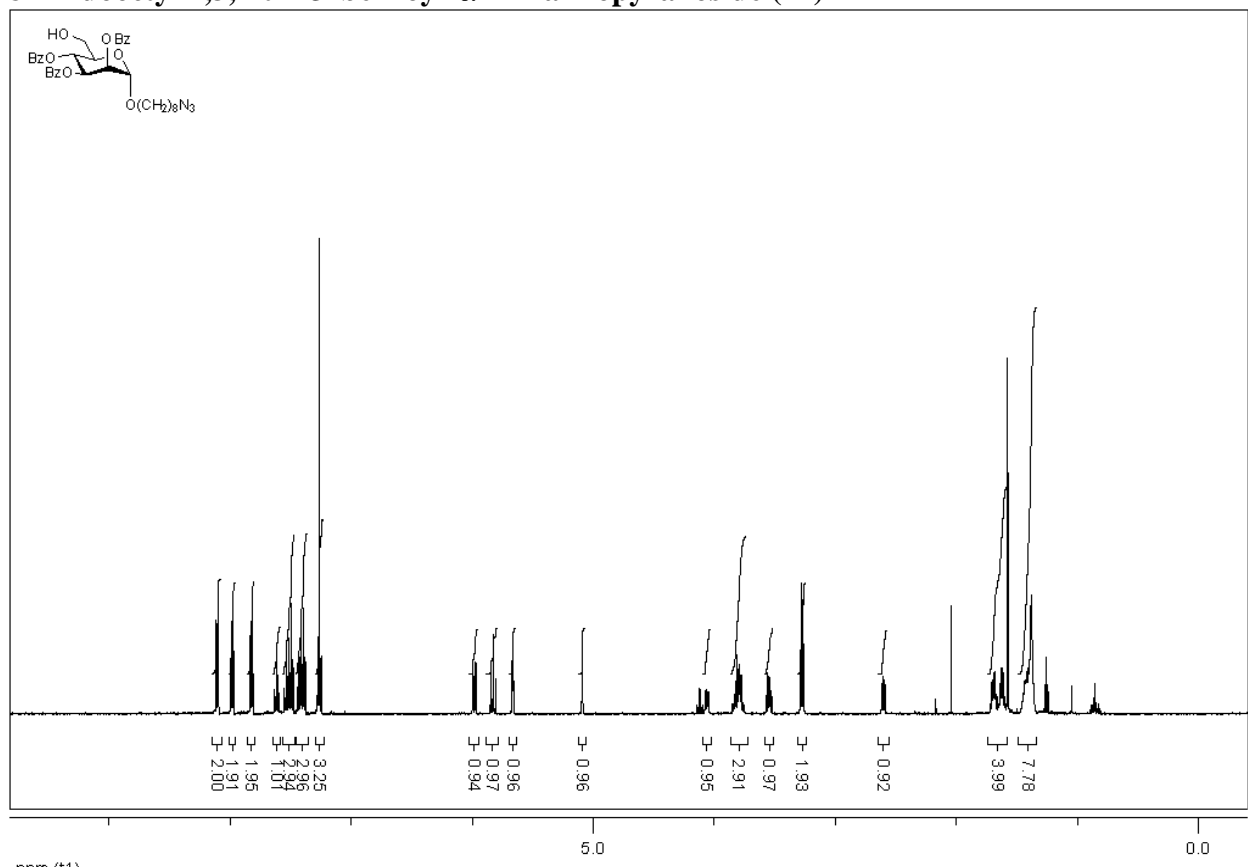
# 8-Azidooctyl 6-O-(tert-butyl-diphenylsilyl)- $\alpha$ -D-mannopyranoside



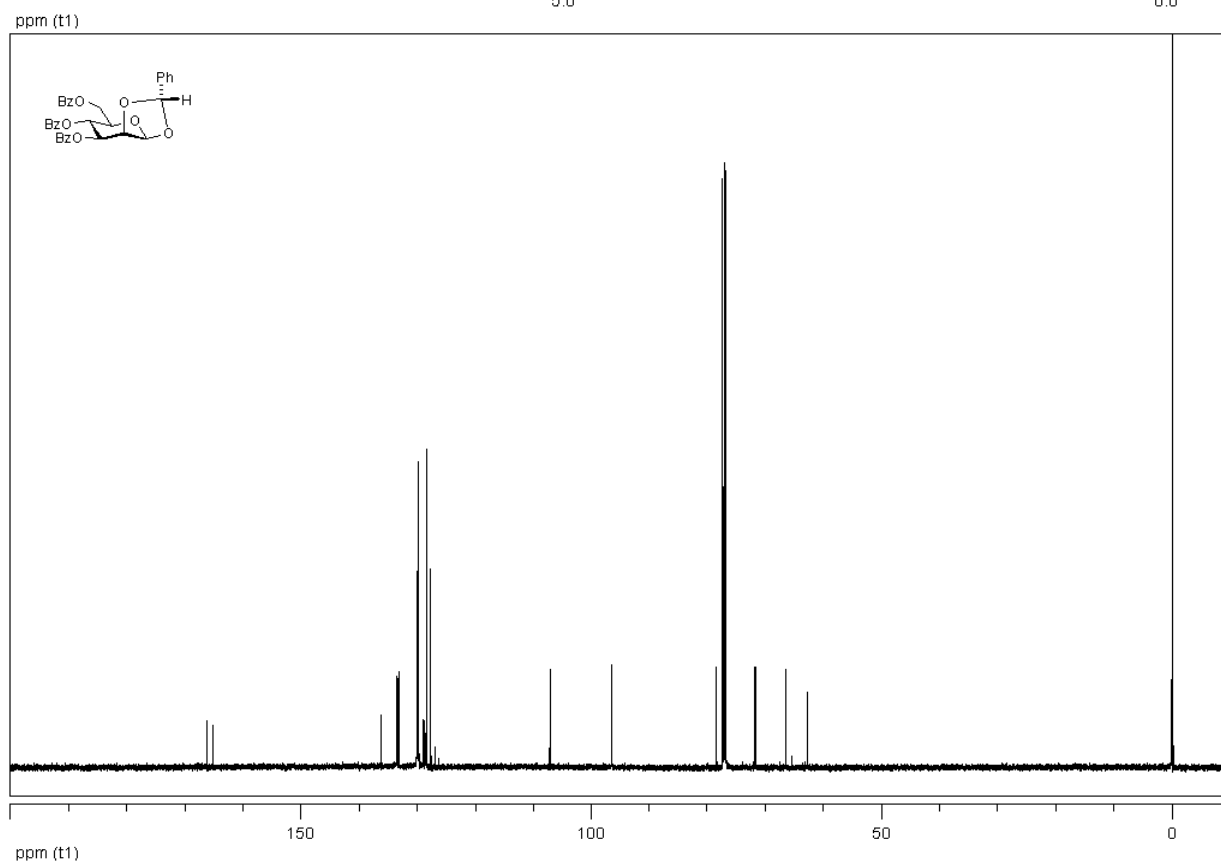
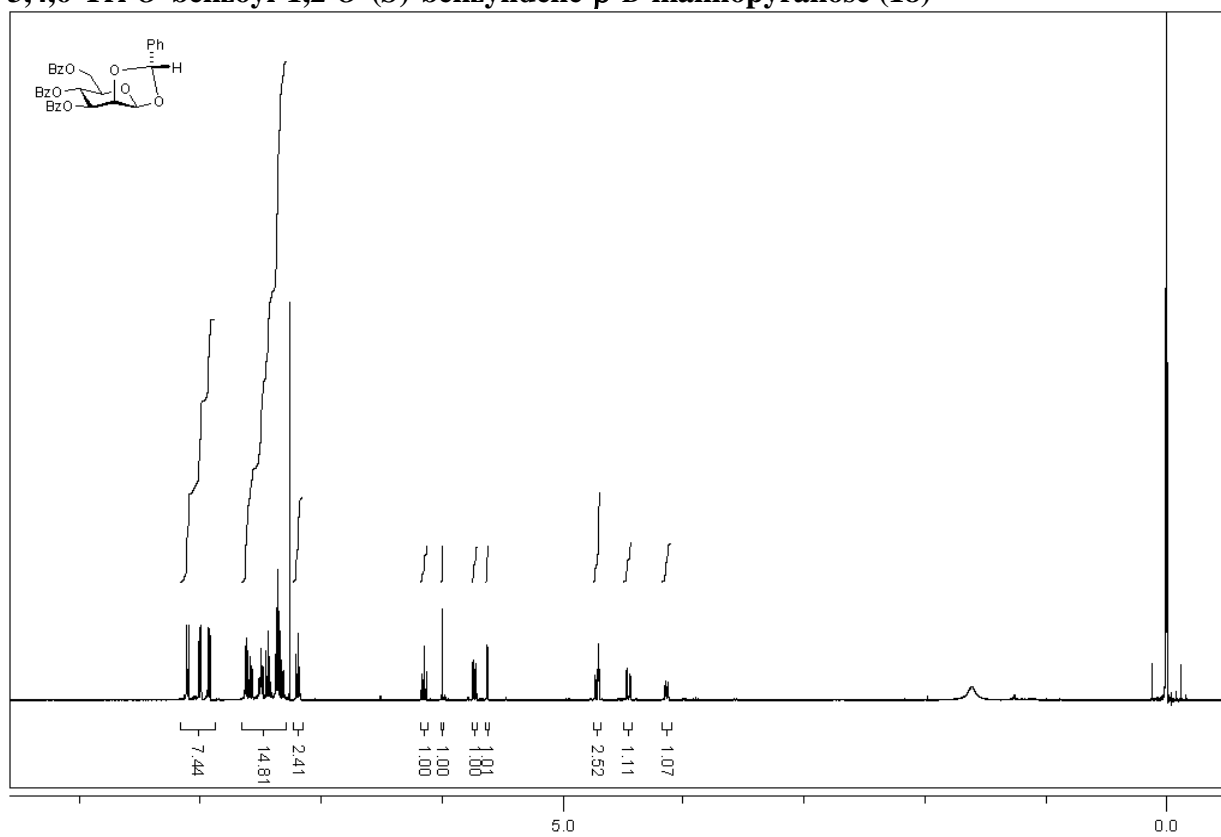
# 8-Azidooctyl 2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)- $\alpha$ -D-mannopyranoside (13)



# 8-Azidoctyl 2,3,4-tri-O-benzoyl- $\alpha$ -D-mannopyranoside (14)

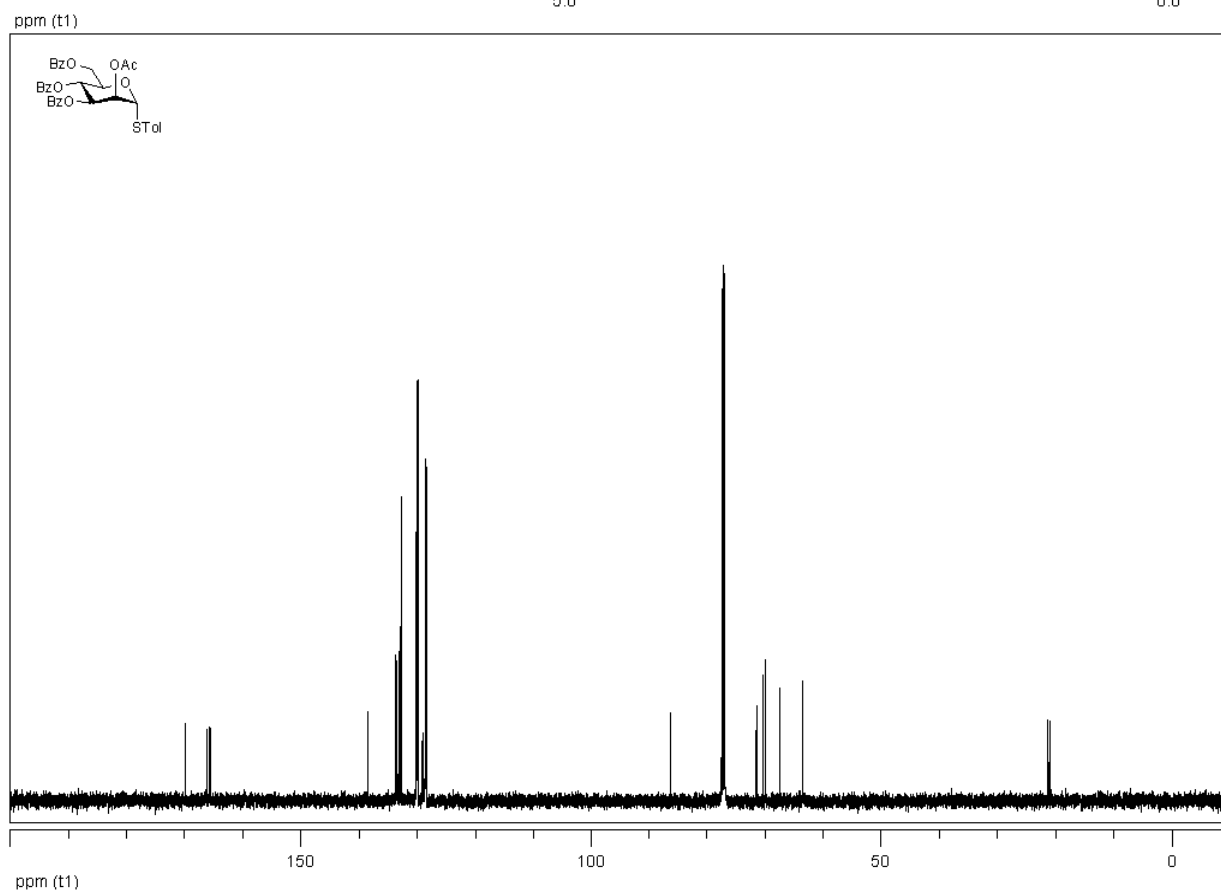
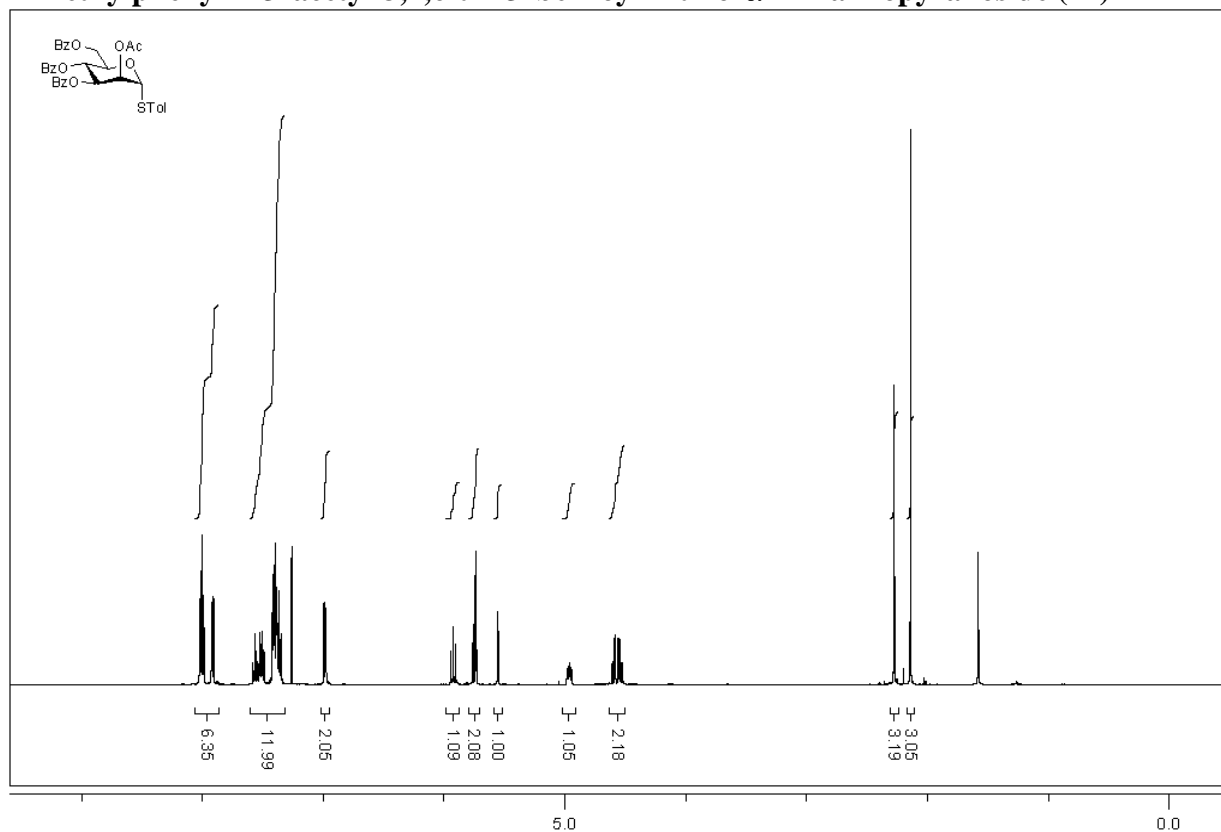


### 3,4,6-Tri-*O*-benzoyl-1,2-*O*-(*S*)-benzylidene- $\beta$ -D-mannopyranose (18)

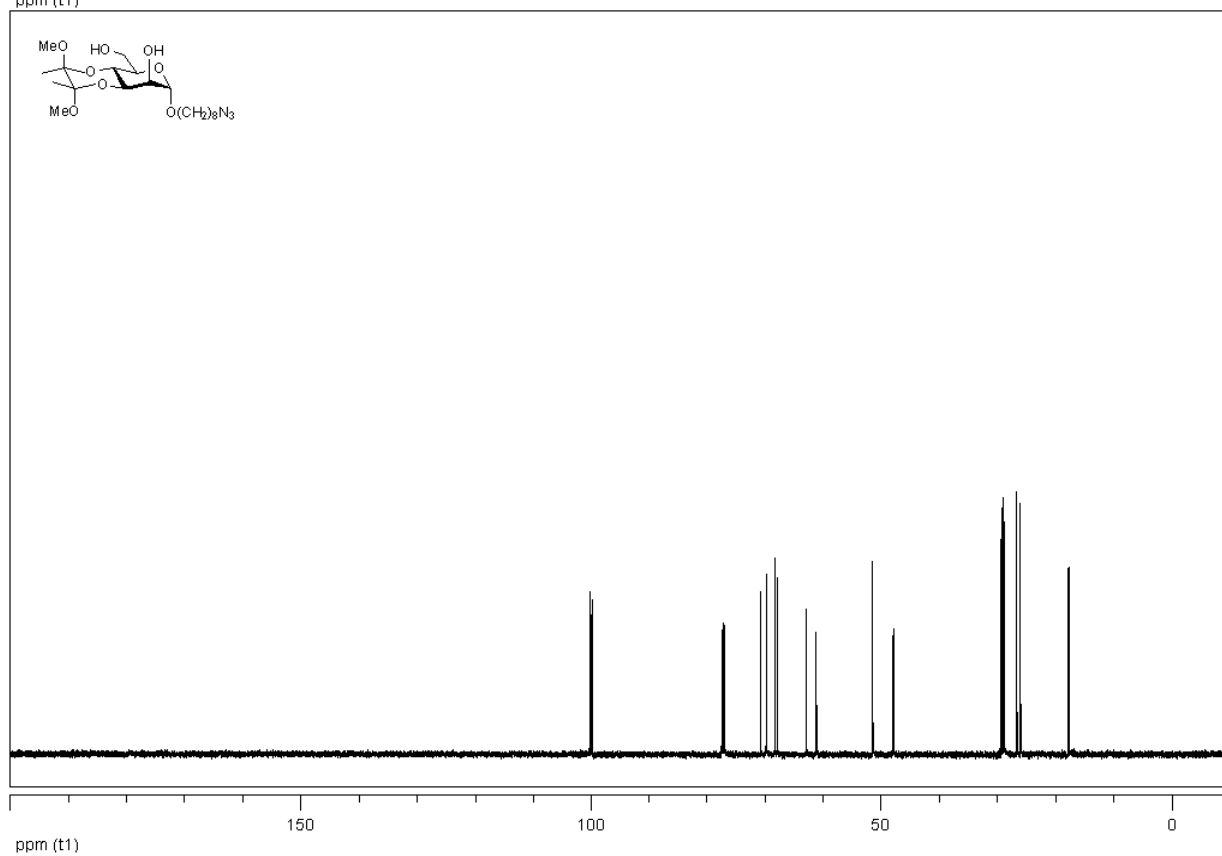
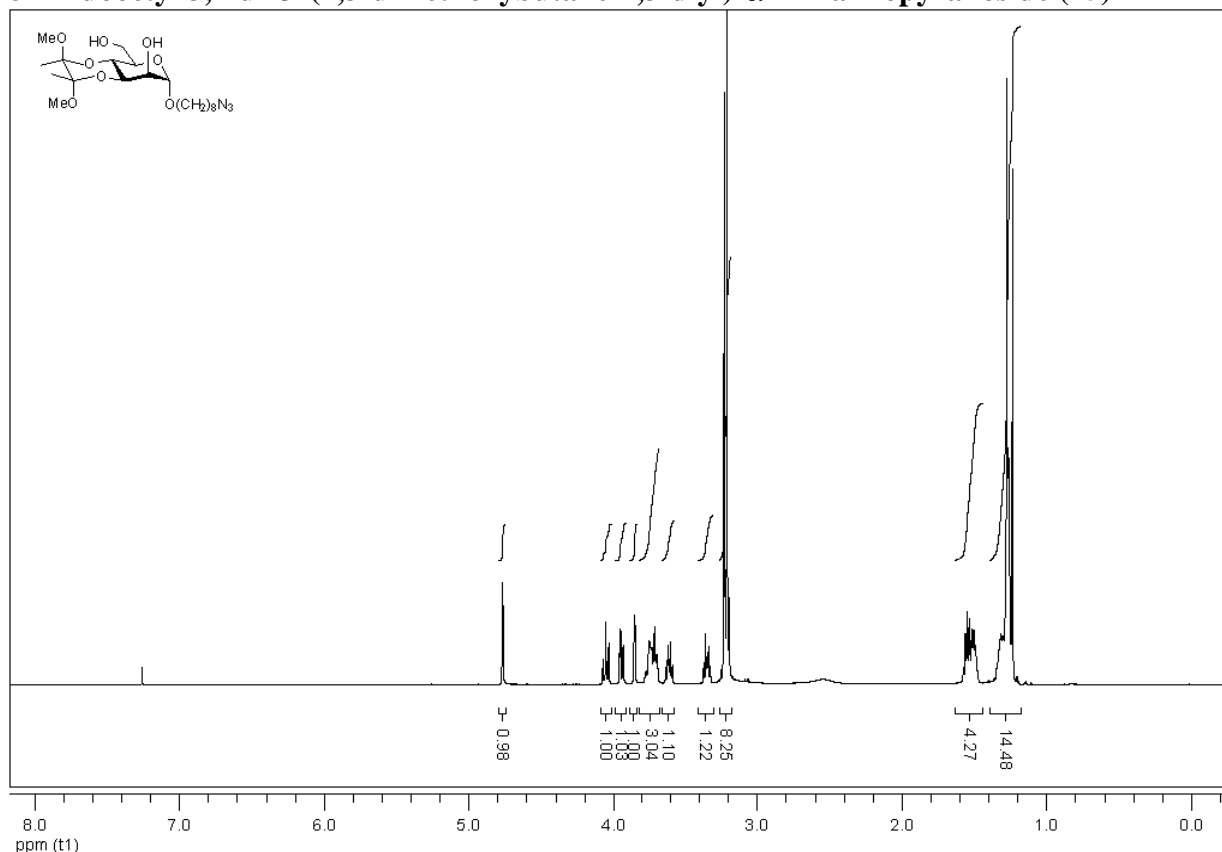




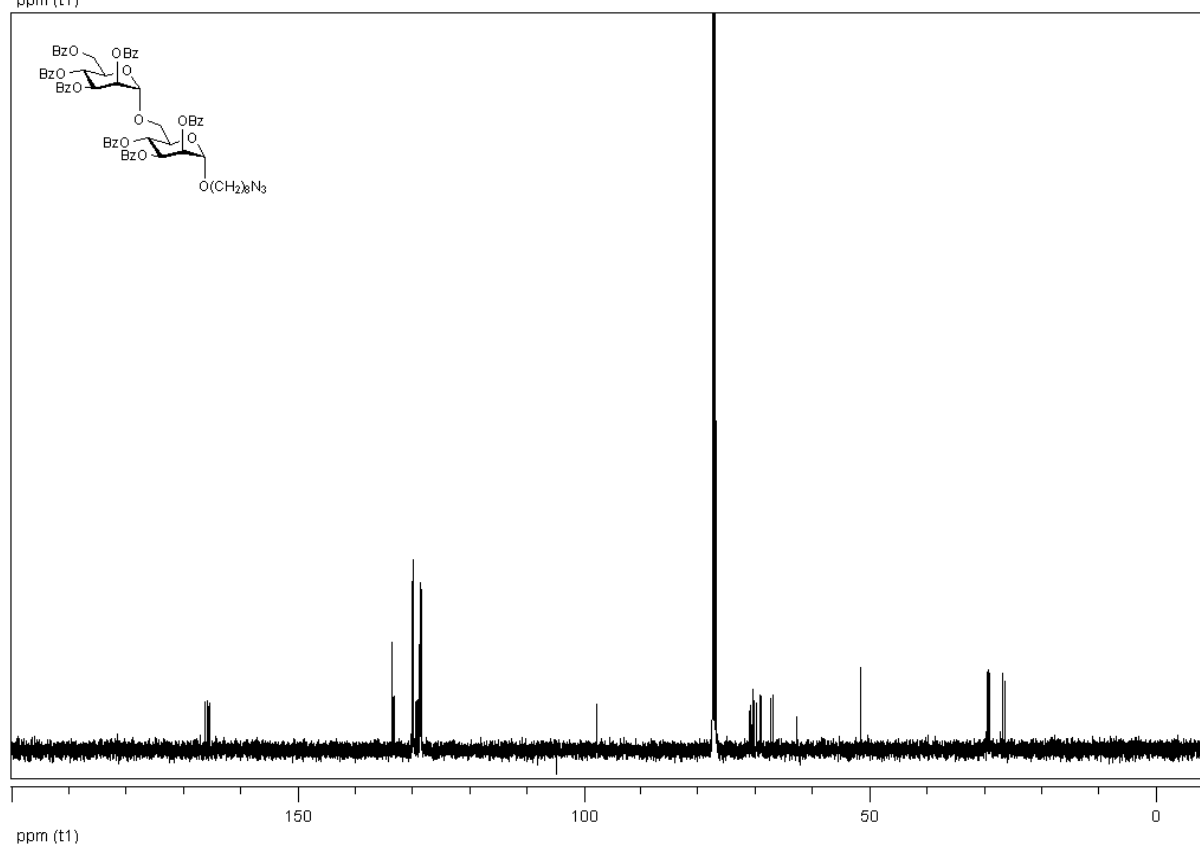
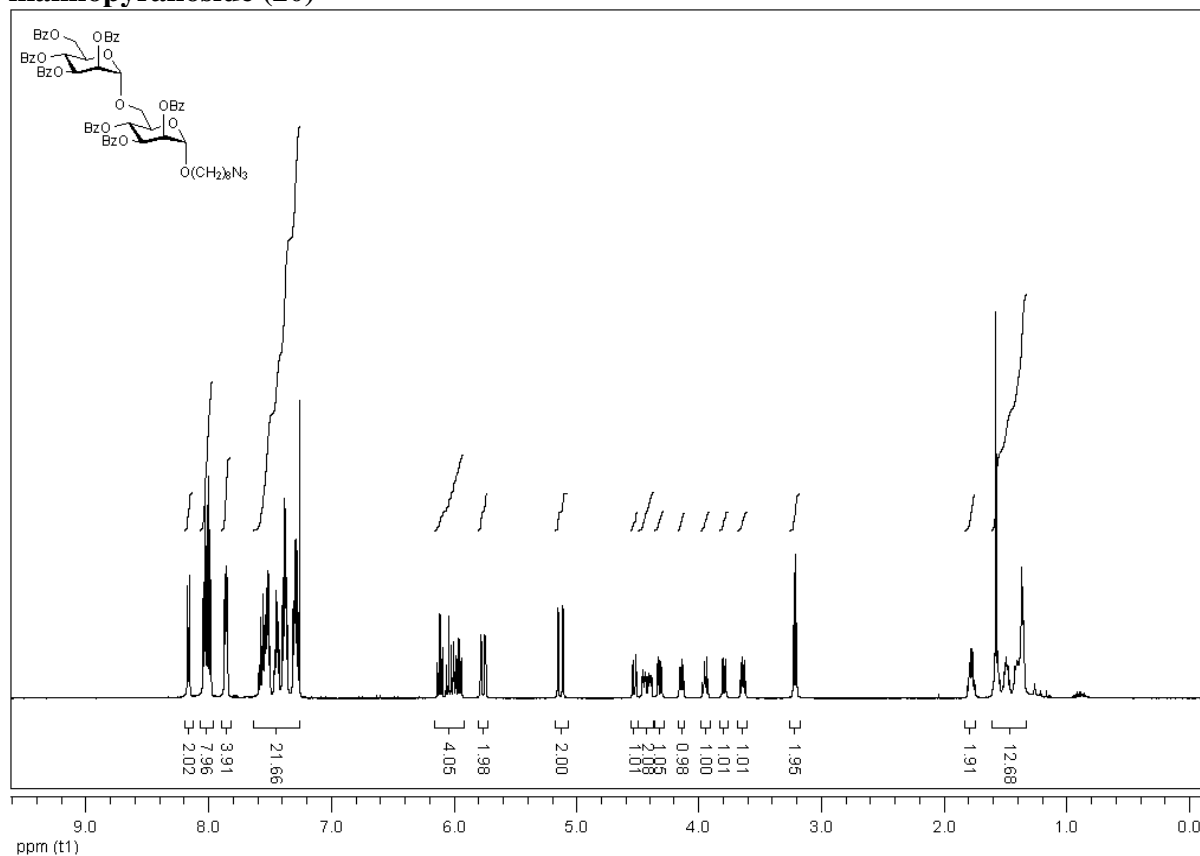
### 4-Methylphenyl 2-O-acetyl-3,4,6-tri-O-benzoyl-1-thio- $\alpha$ -D-mannopyranoside (17)



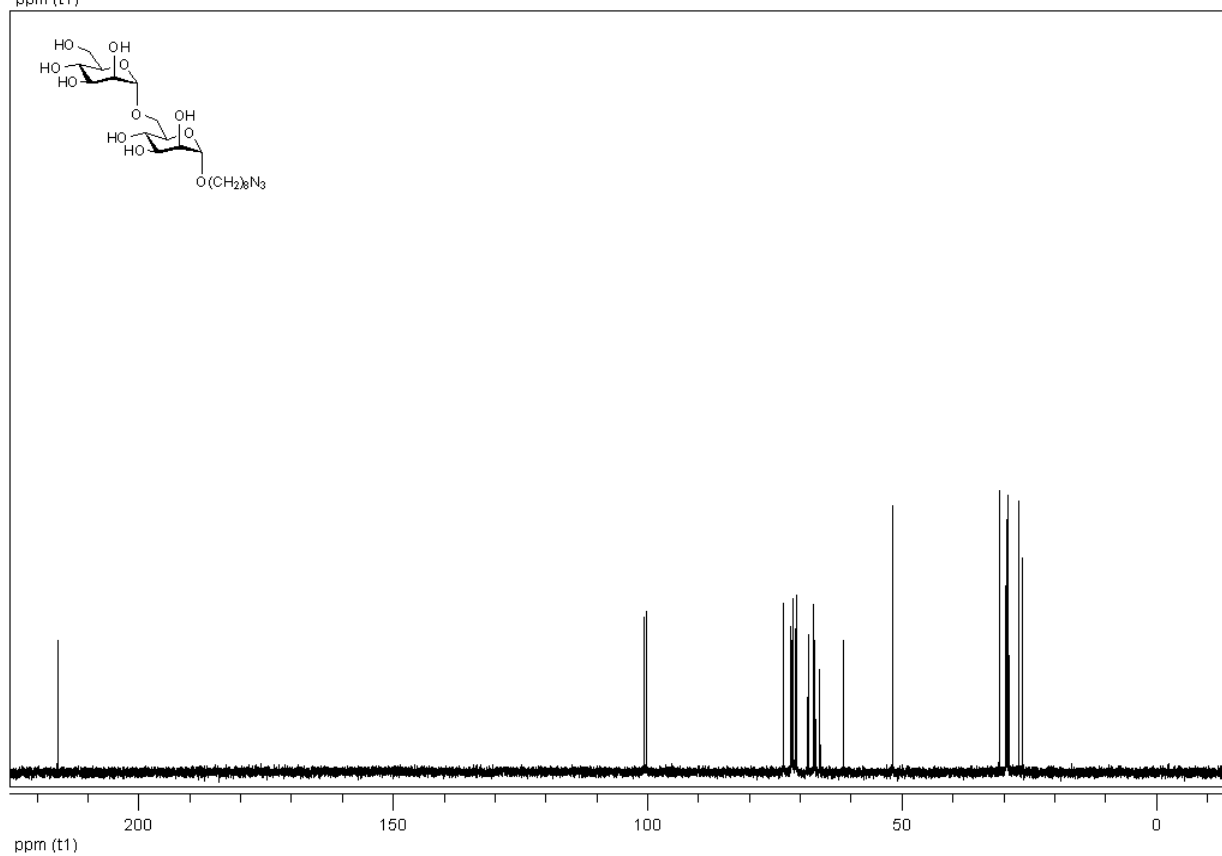
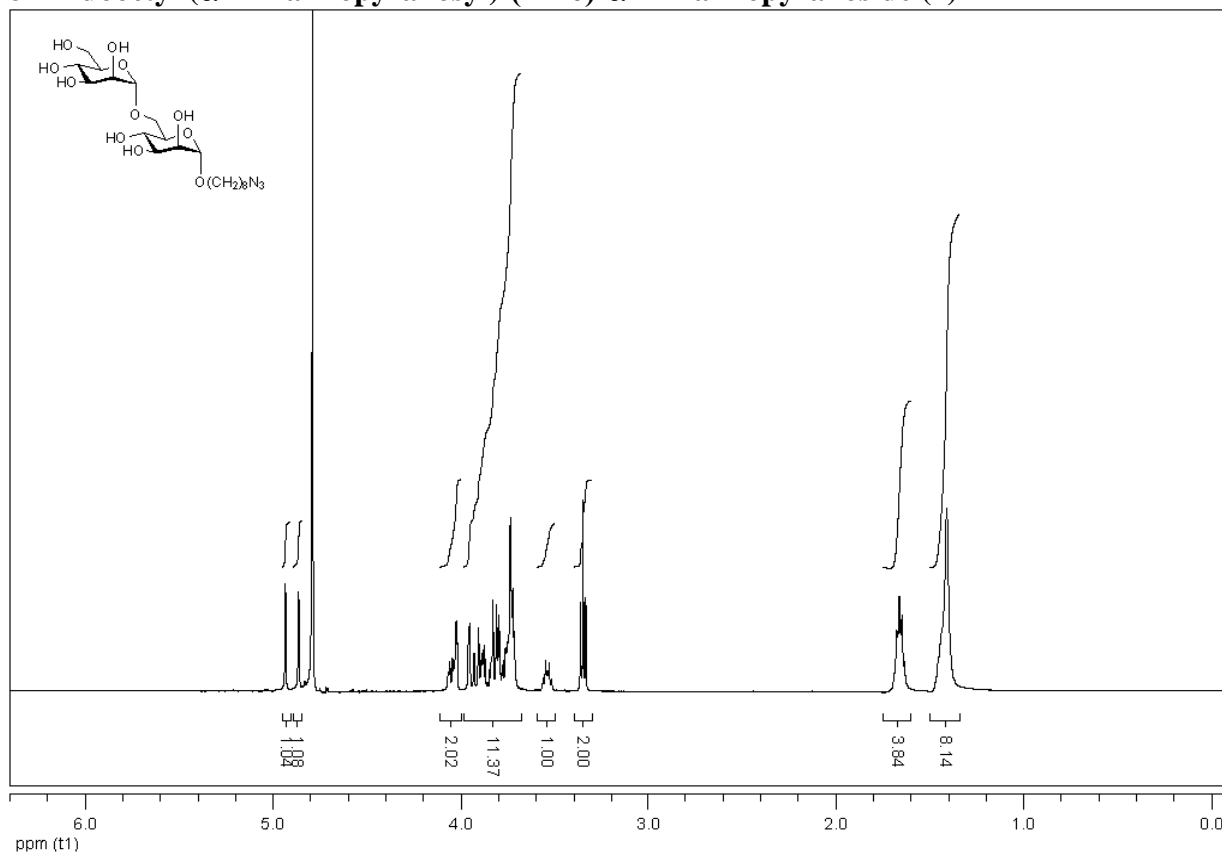
### 8-Azidooctyl 3,4-di-O-(2,3-dimethoxybutane-2,3-diyl)- $\alpha$ -D-mannopyranoside (15)



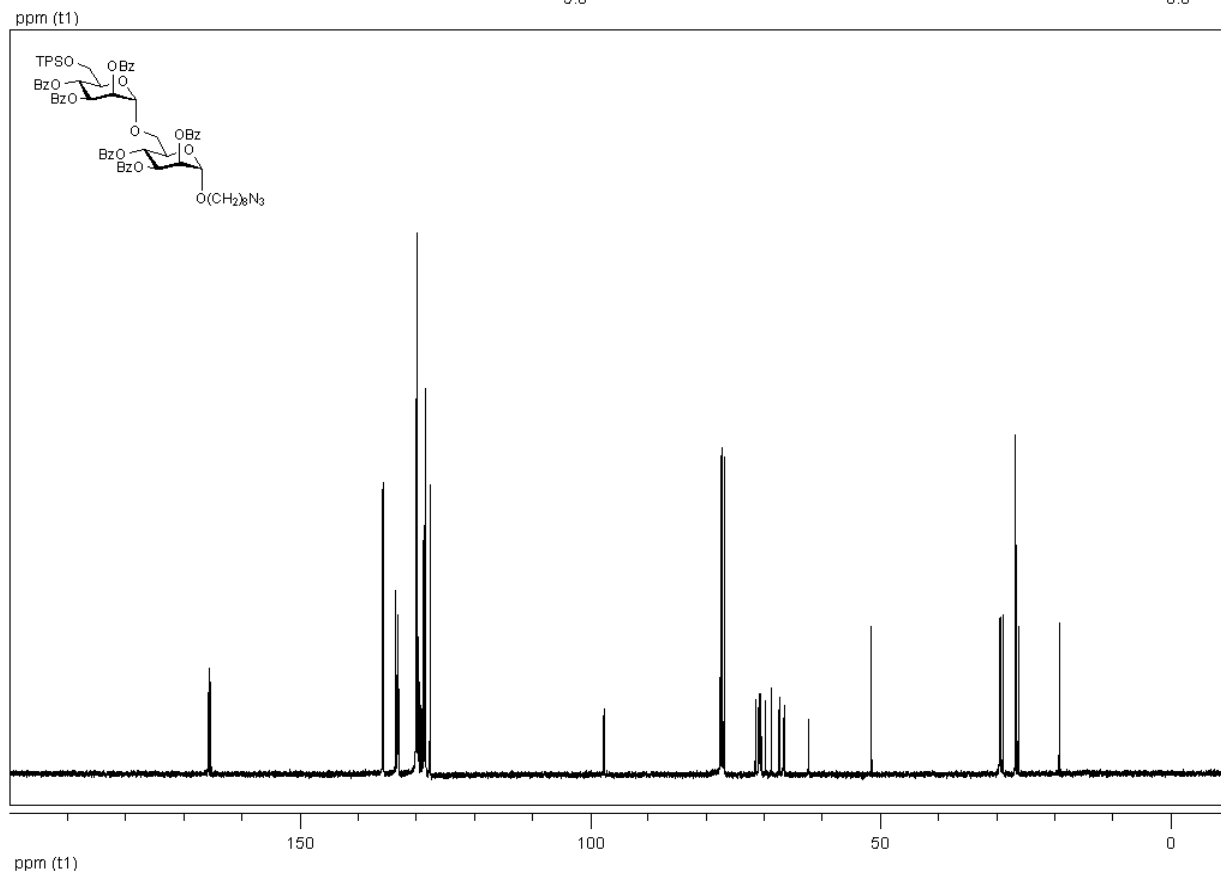
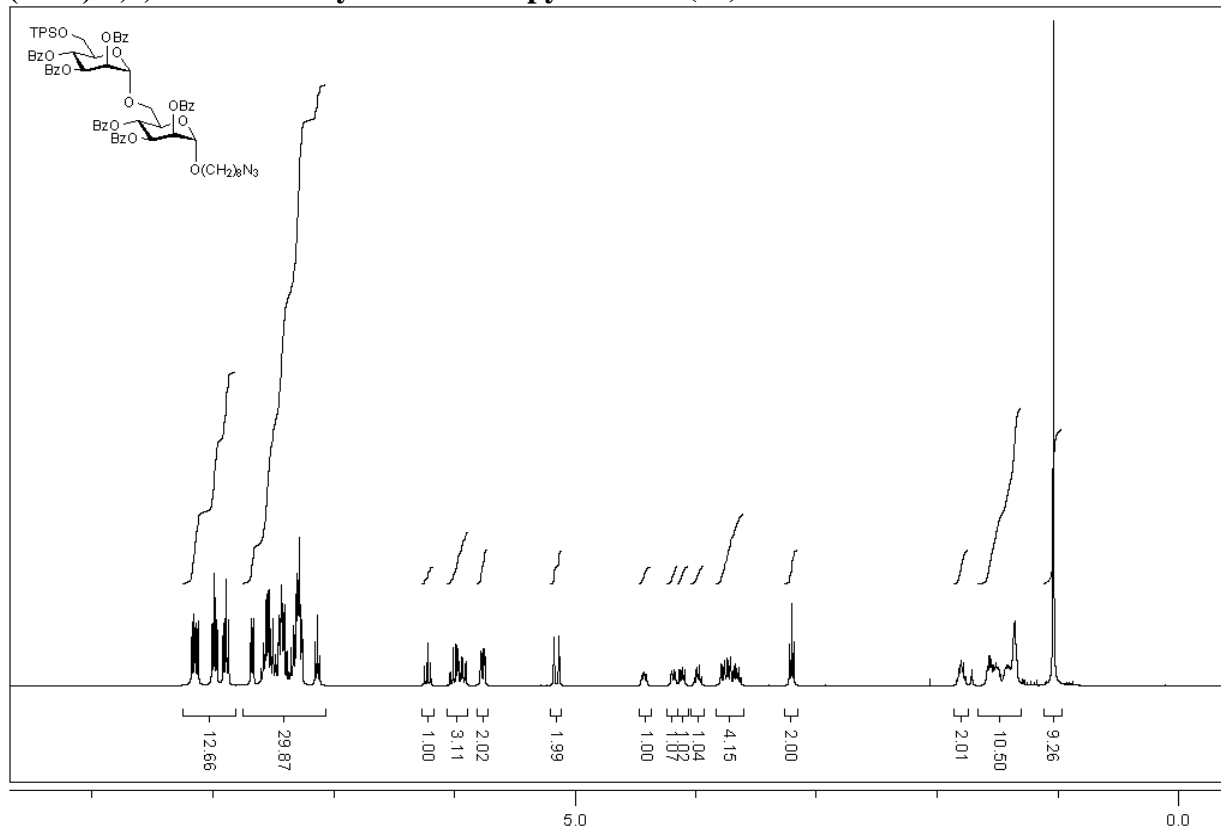
**8-Azidooctyl (2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranoside (20)**



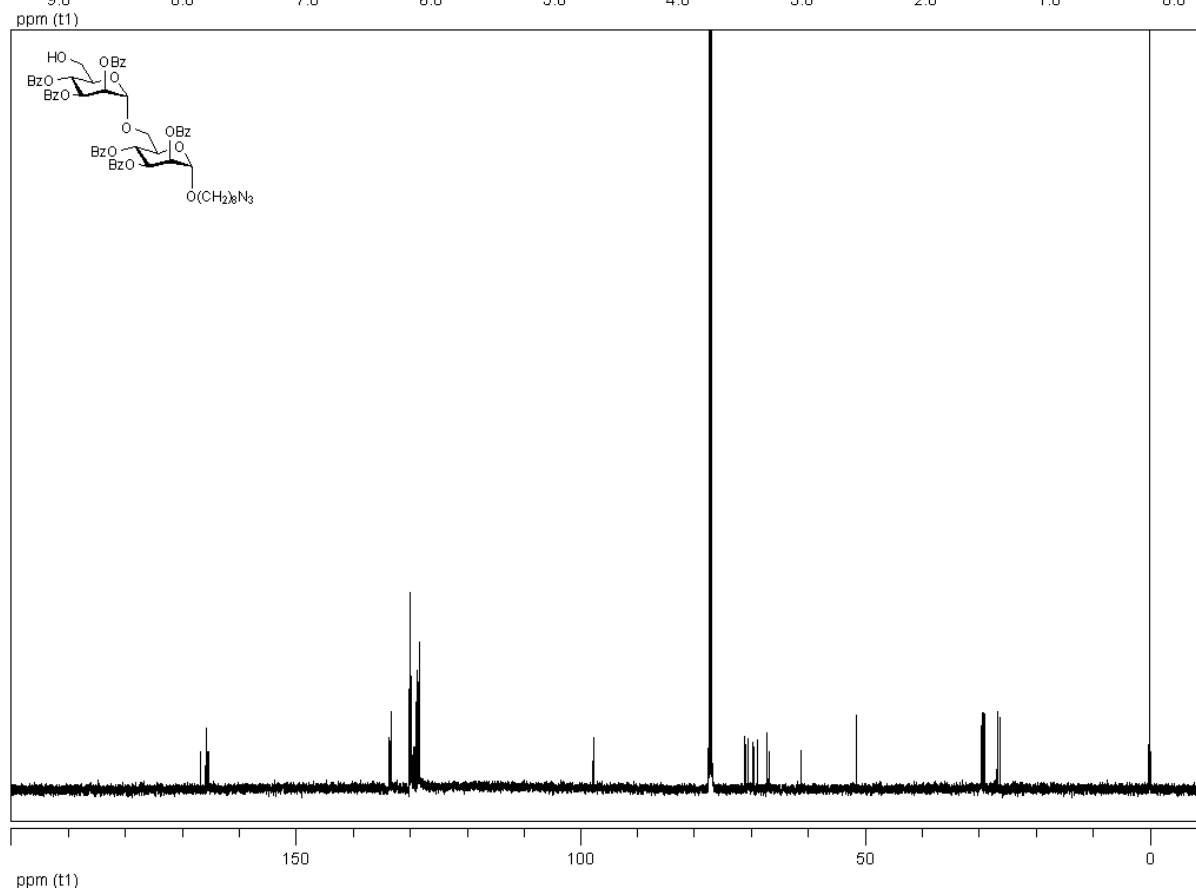
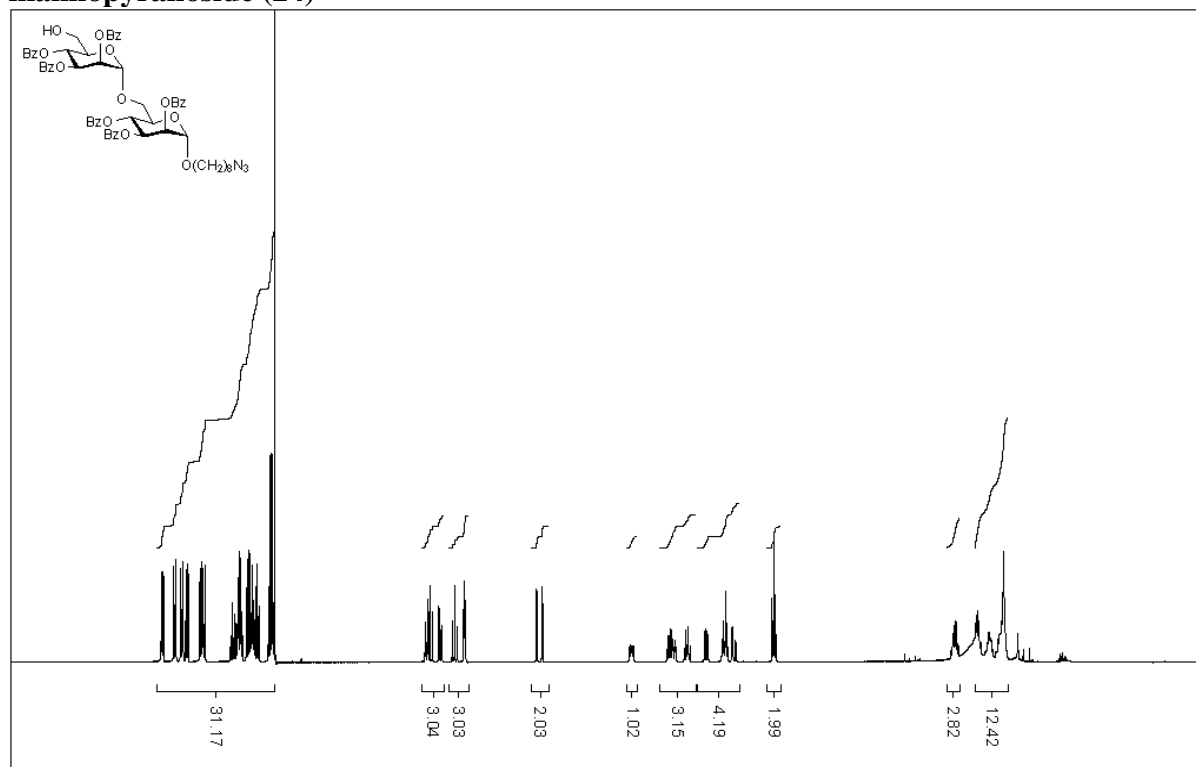
### 8-Azidoethyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (1)



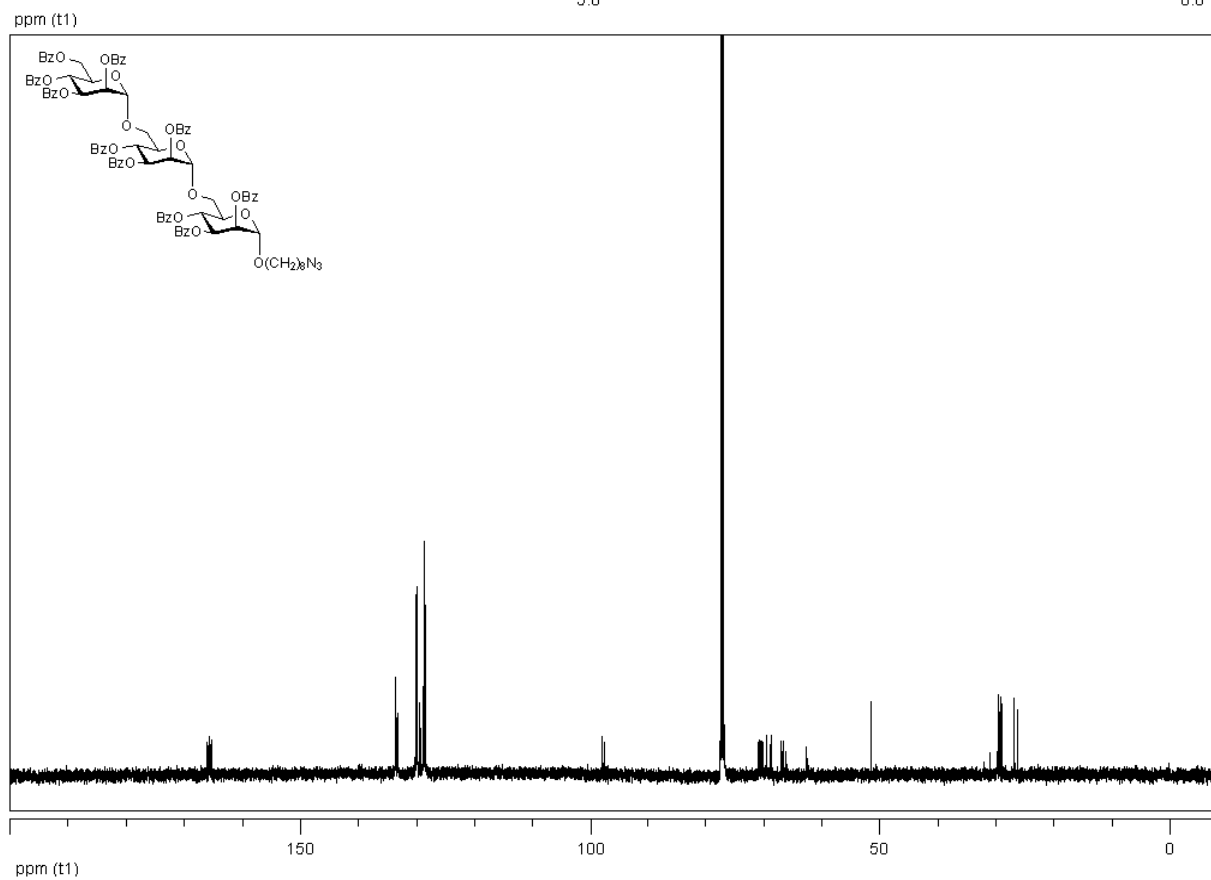
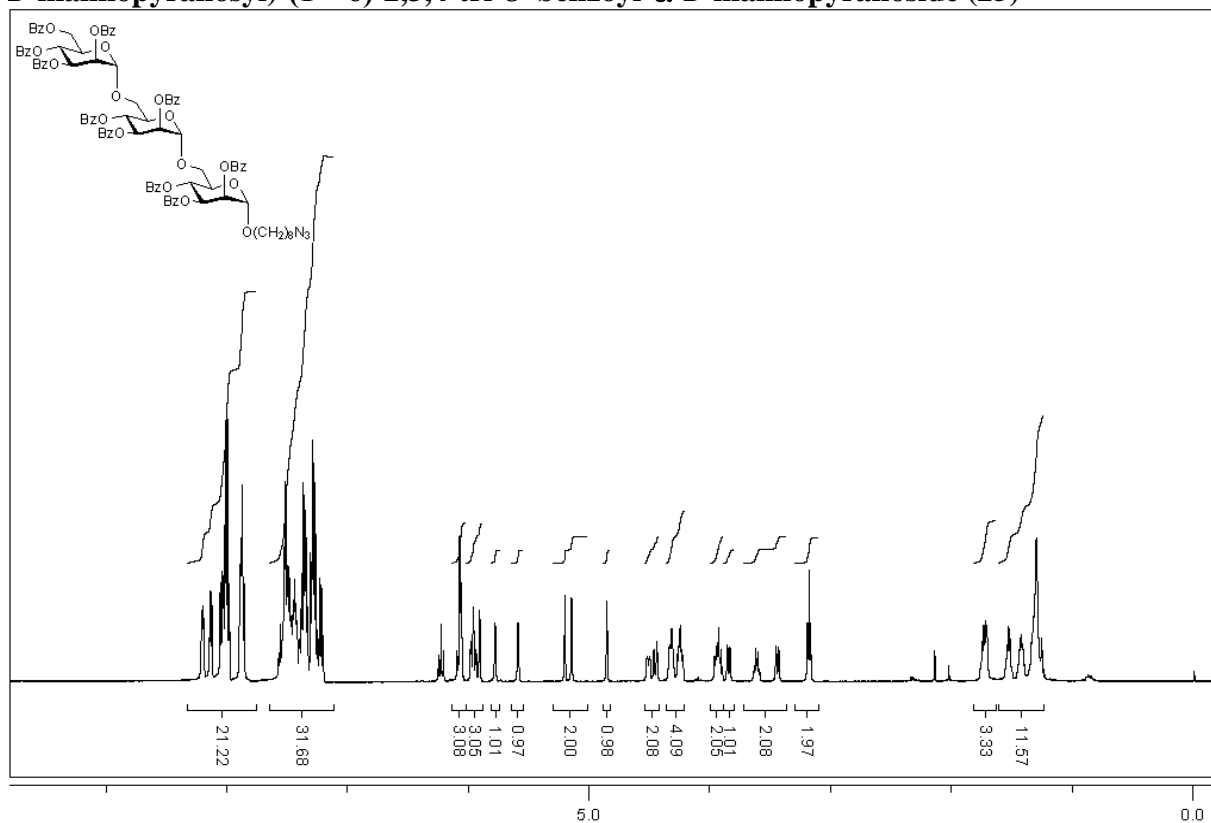
**8-Azidoctyl (2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranoside (23)**



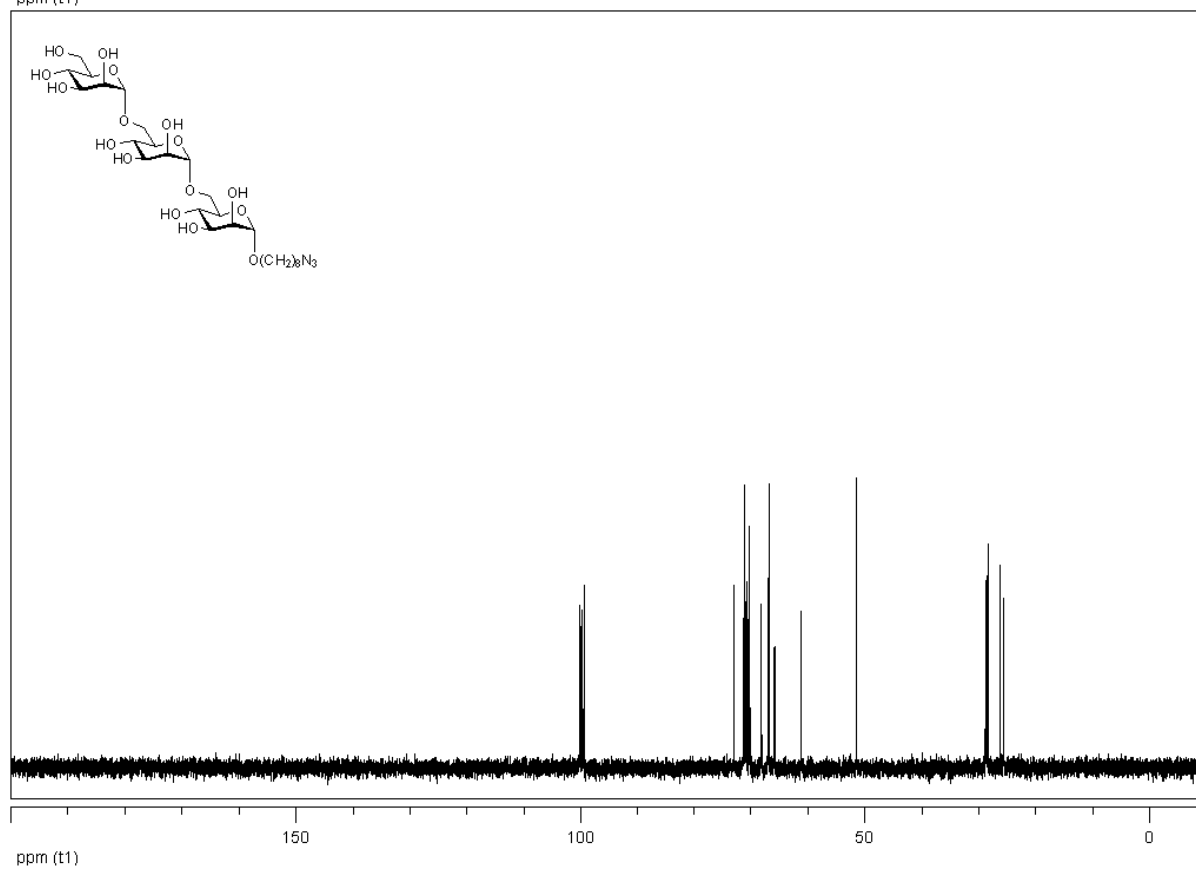
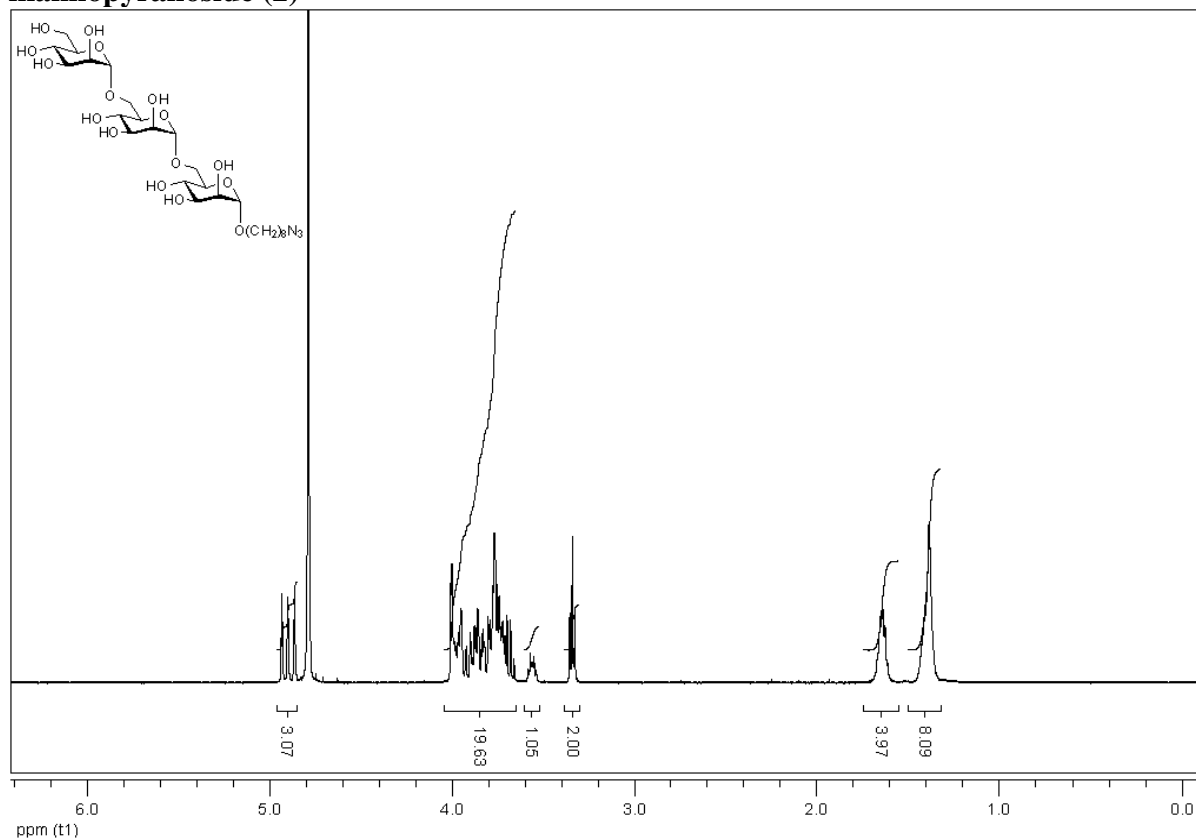
**8-Azidooctyl (2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranoside (24)**



**8-Azido-octyl (2,3,4,6-tetra-O-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-(2,3,4-tri-O-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-O-benzoyl- $\alpha$ -D-mannopyranoside (25)**

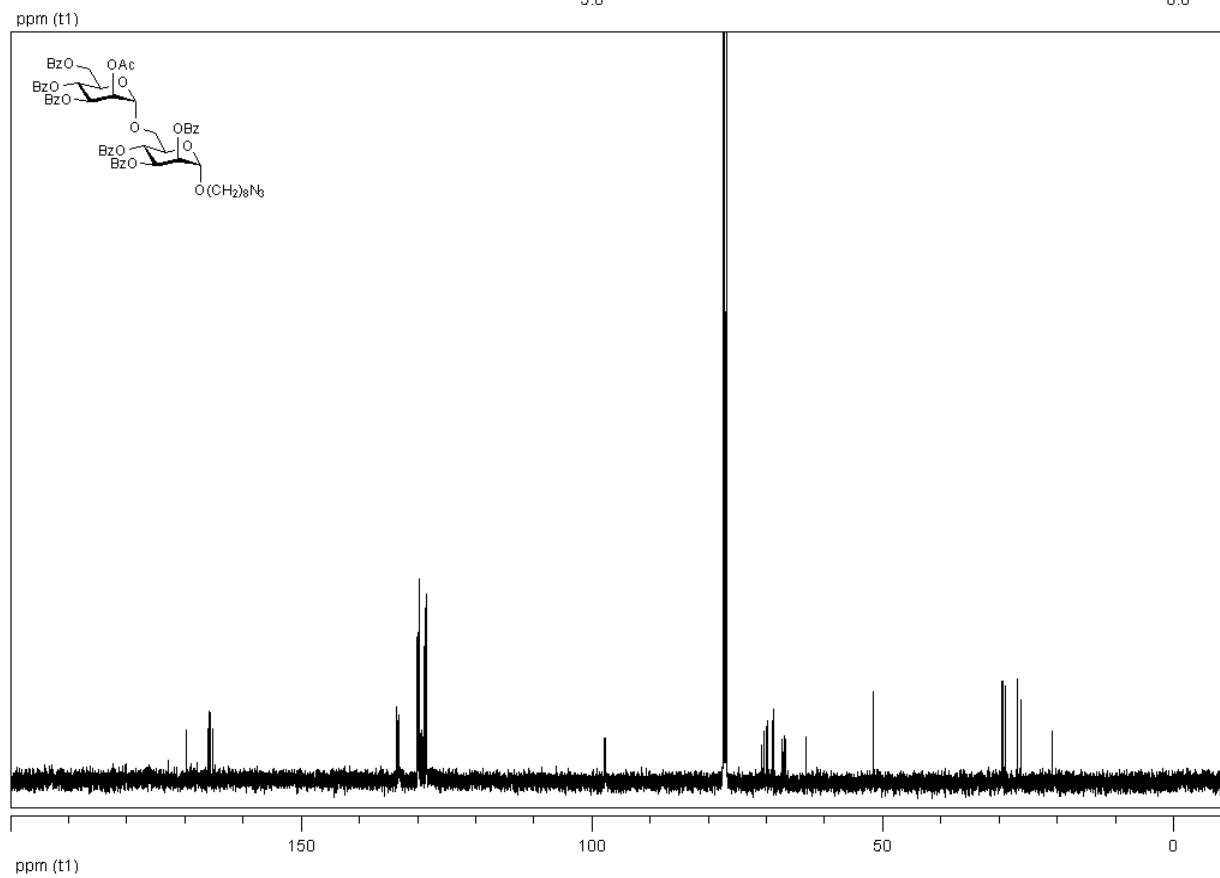
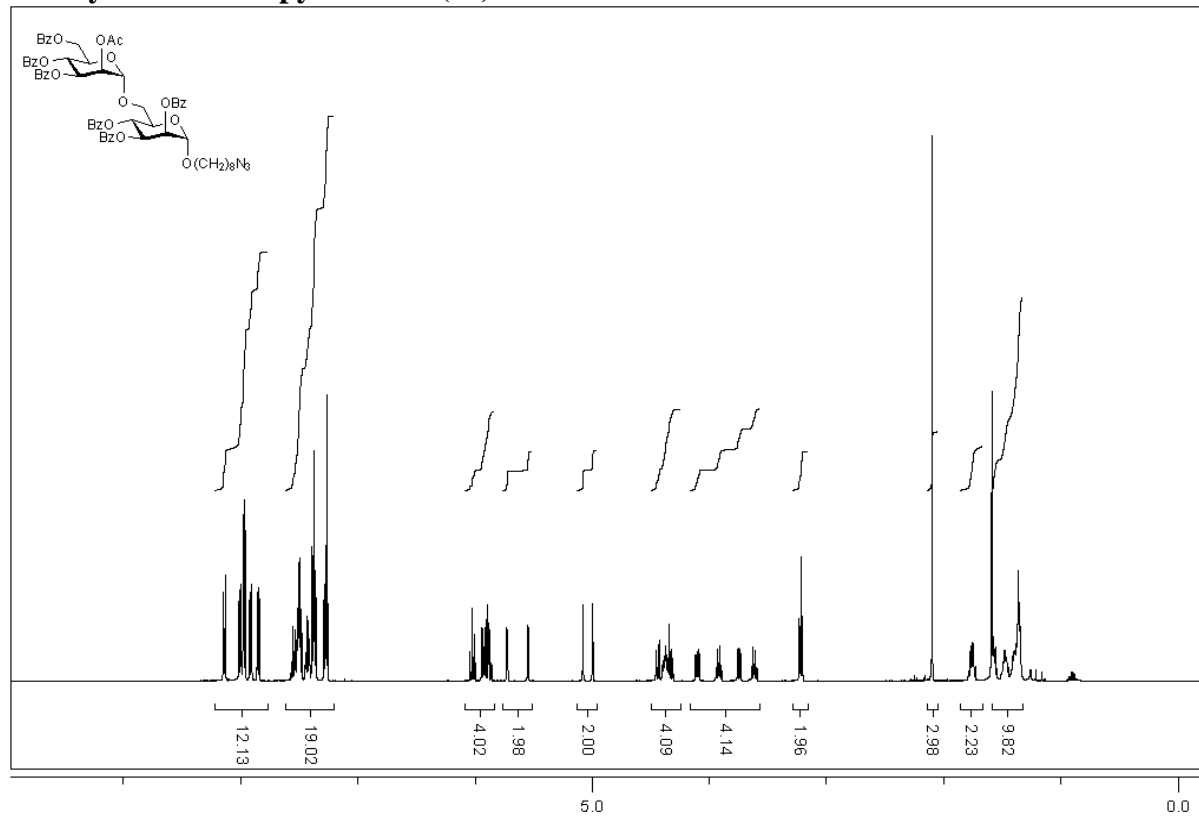


**8-Azidoethyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (2)**

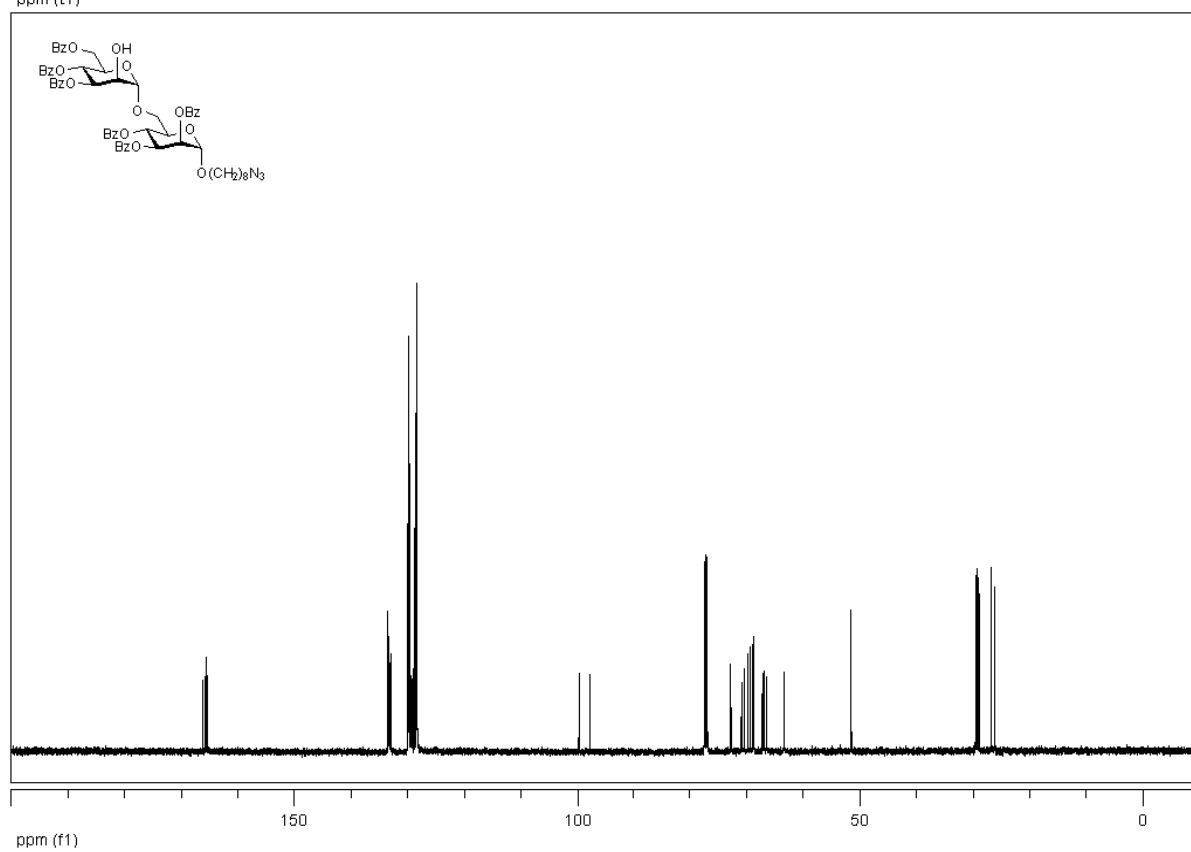
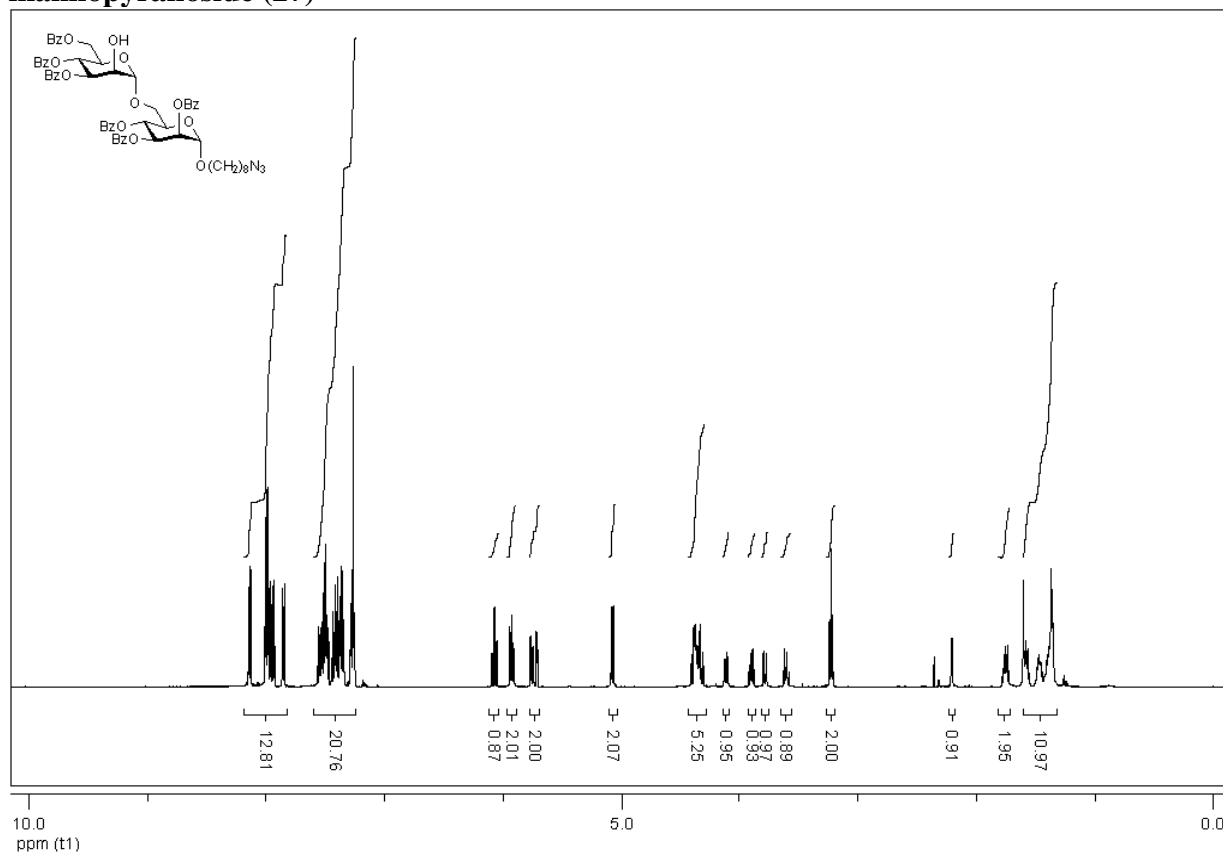




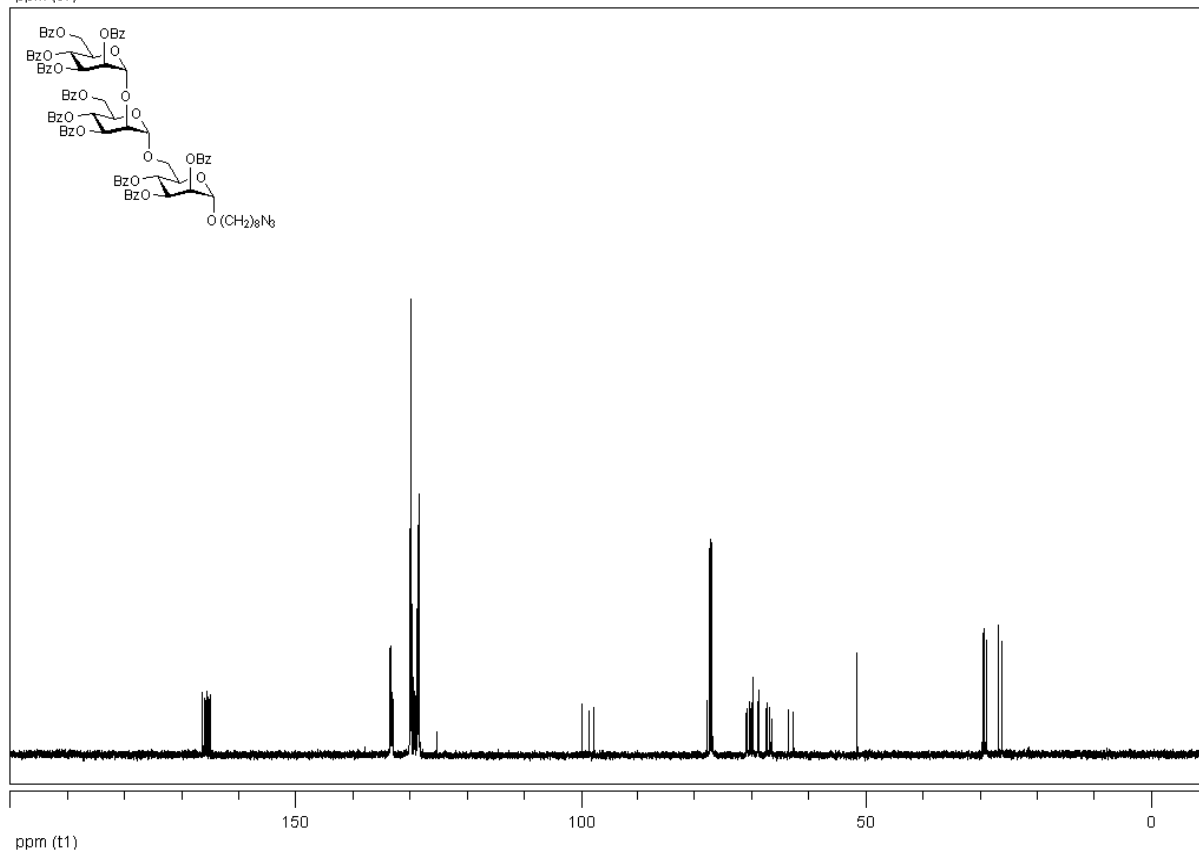
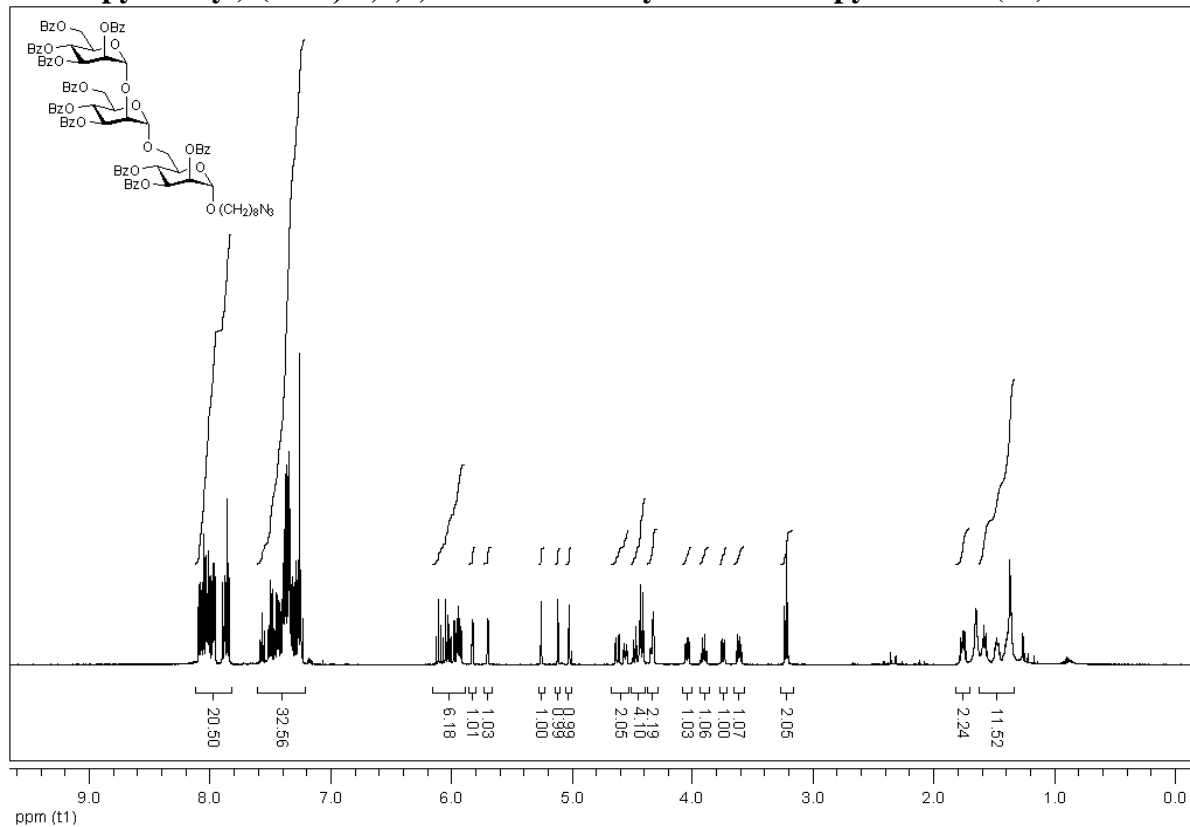
**8-Azidooctyl (2-*O*-acetyl-3,4,6-tri-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranoside (26)**



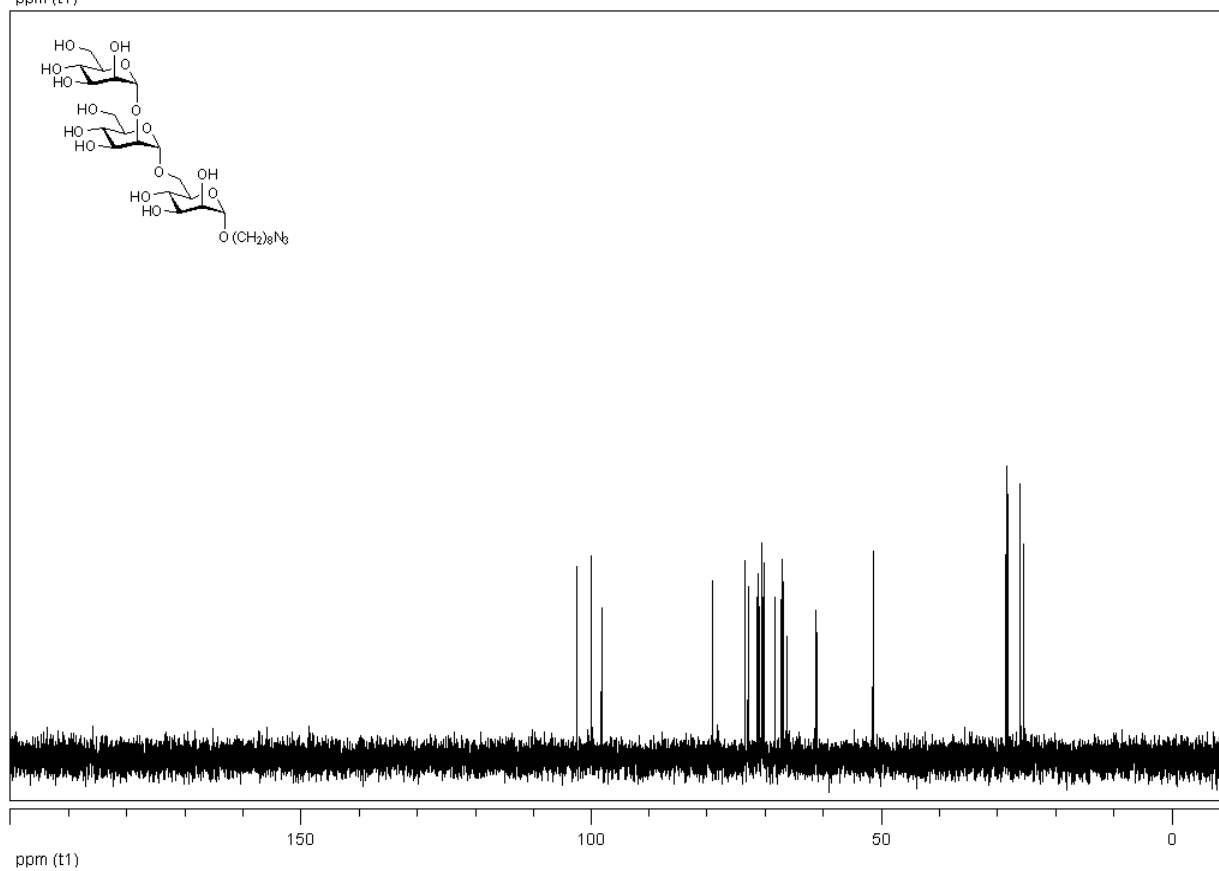
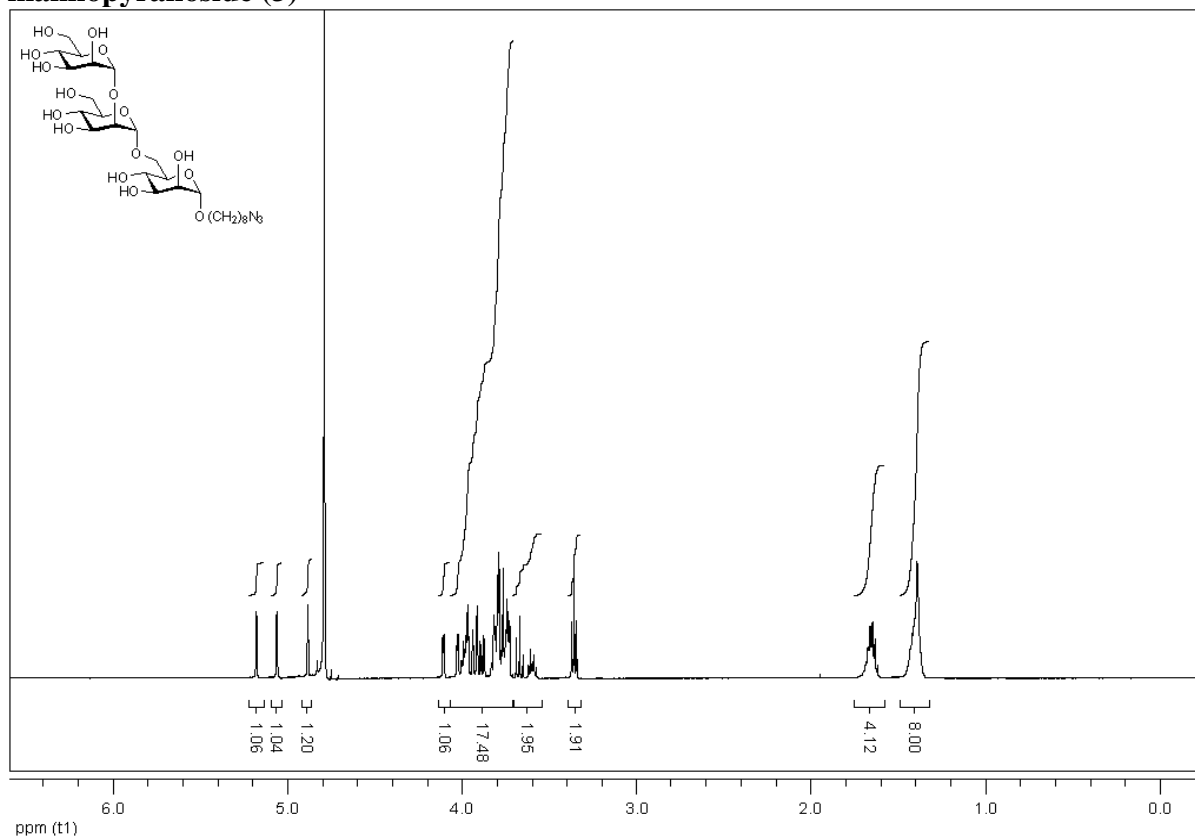
**8-Azidooctyl (3,4,6-tri-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranoside (27)**



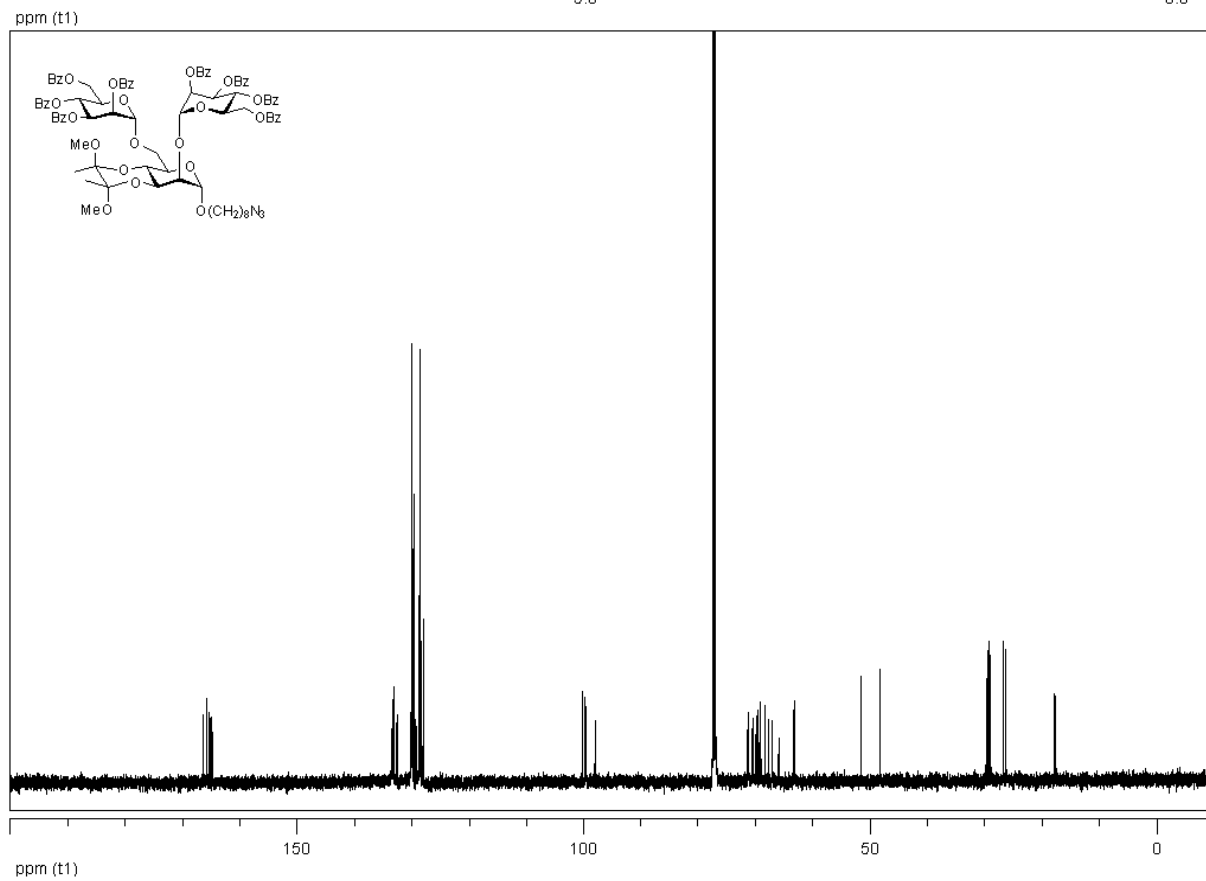
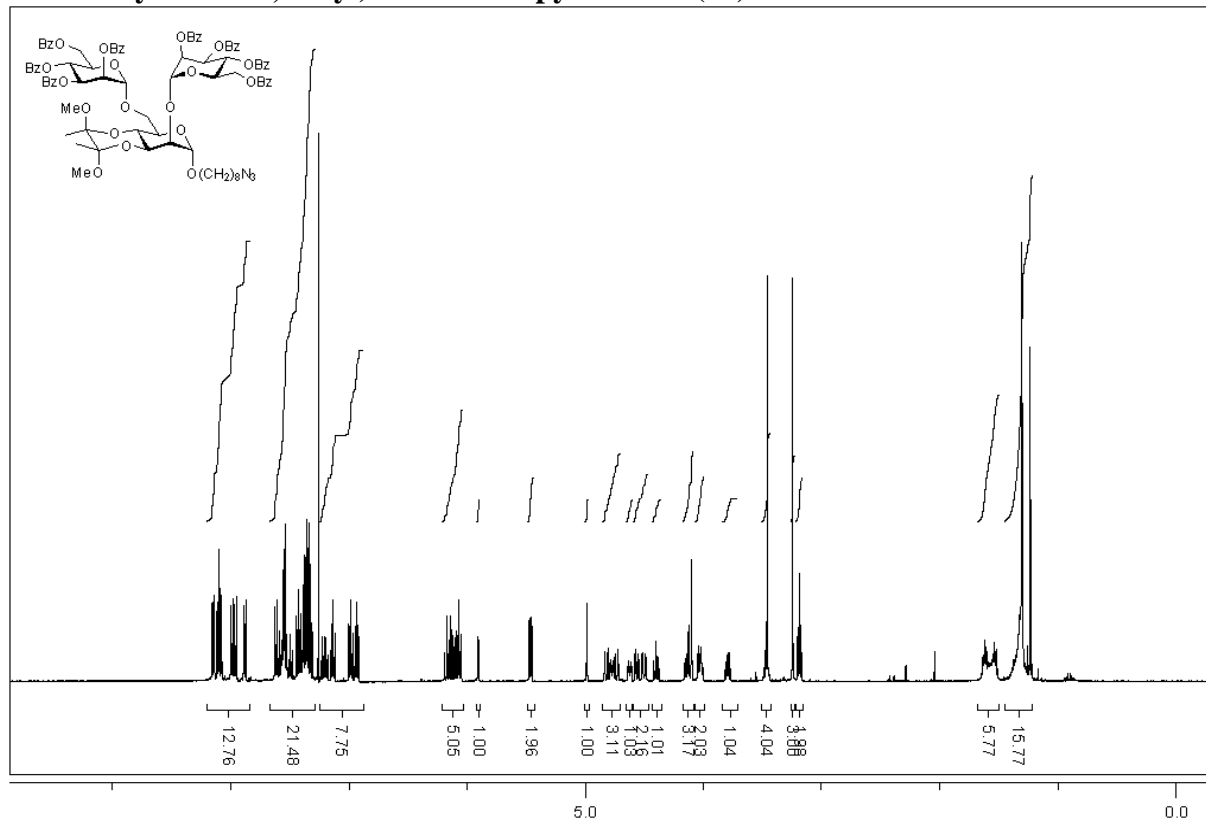
**8-Azidooctyl (2,3,4-tri-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzoyl- $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-mannopyranoside (28)**



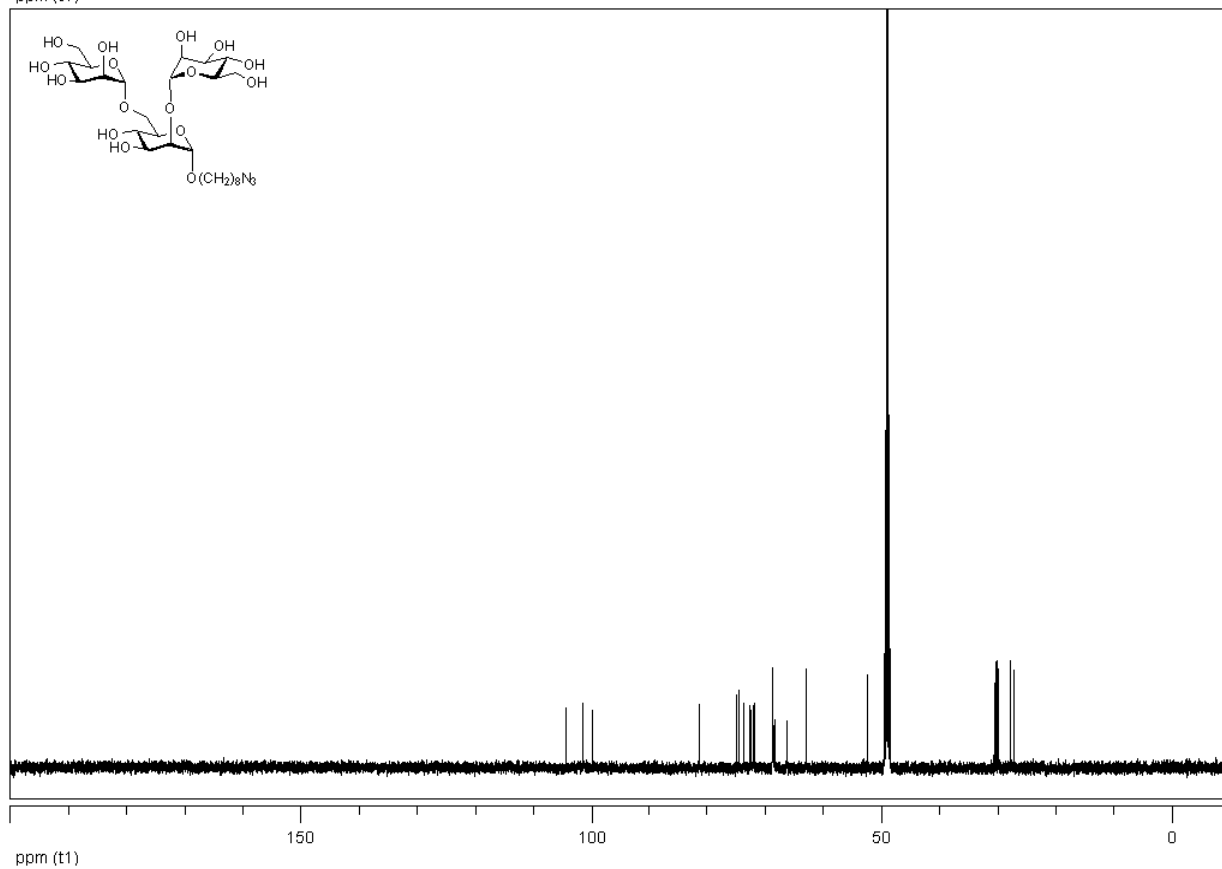
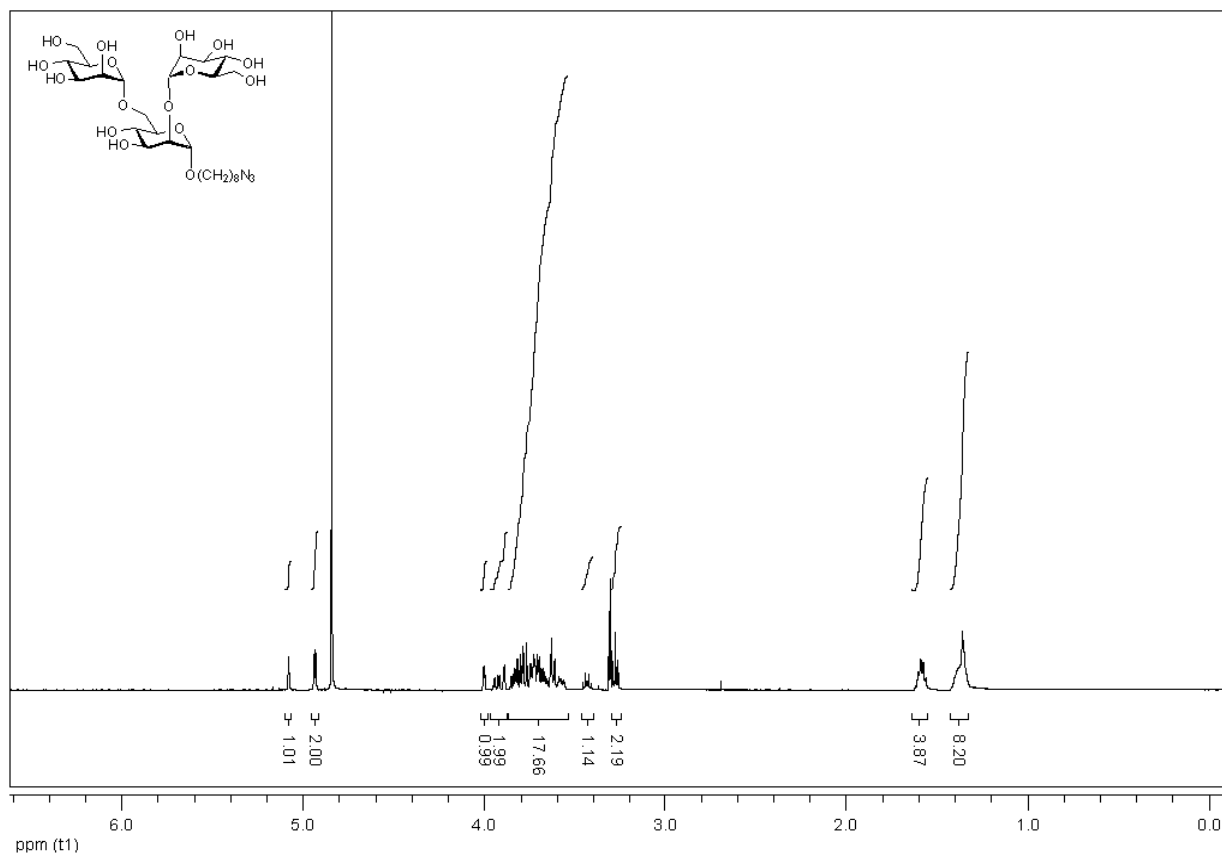
**8-Azidooctyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 2)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (3)**



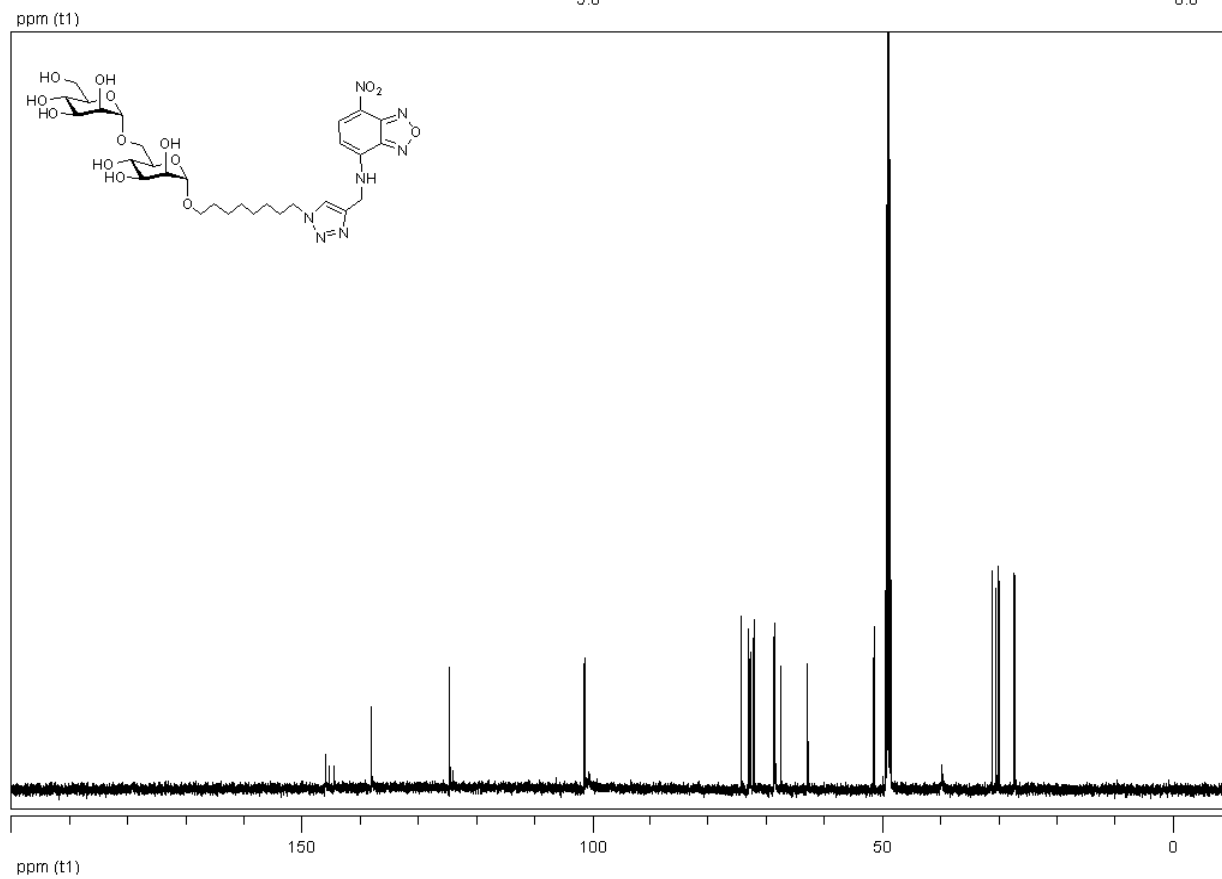
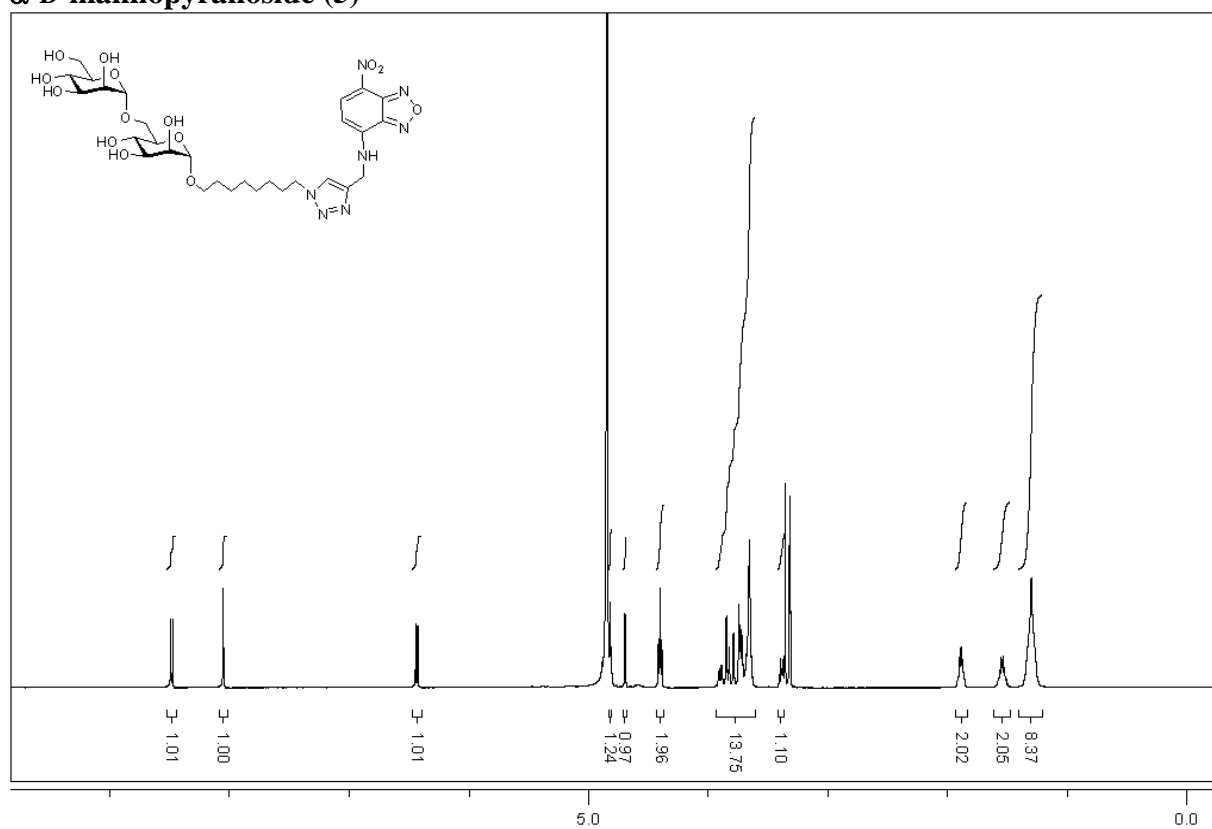
**Azidoethyl 2,6-di-O-(2,3,4,6-tetra-O-benzoyl- $\alpha$ -D-mannopyranosyl)-3,4-di-O-(2,3-dimethoxybutane-2,3-diyl)- $\alpha$ -D-mannopyranoside (29)**



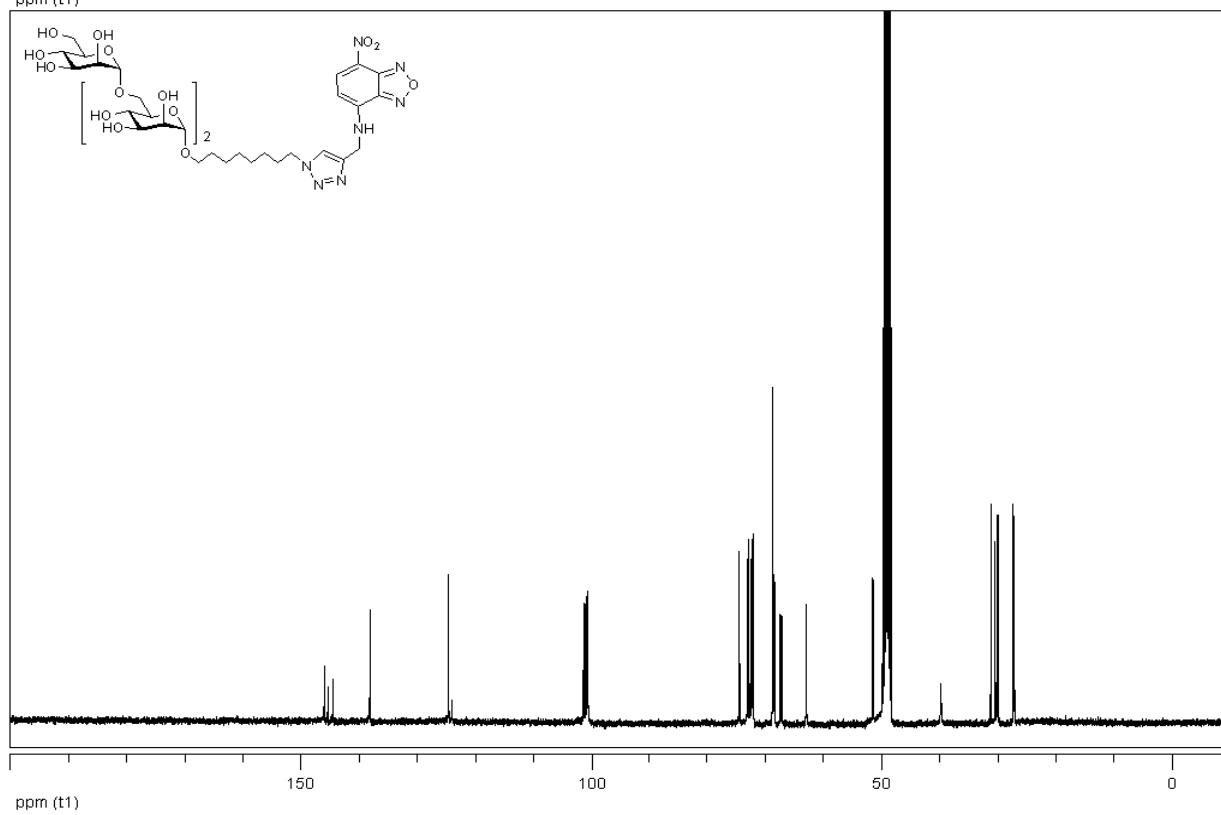
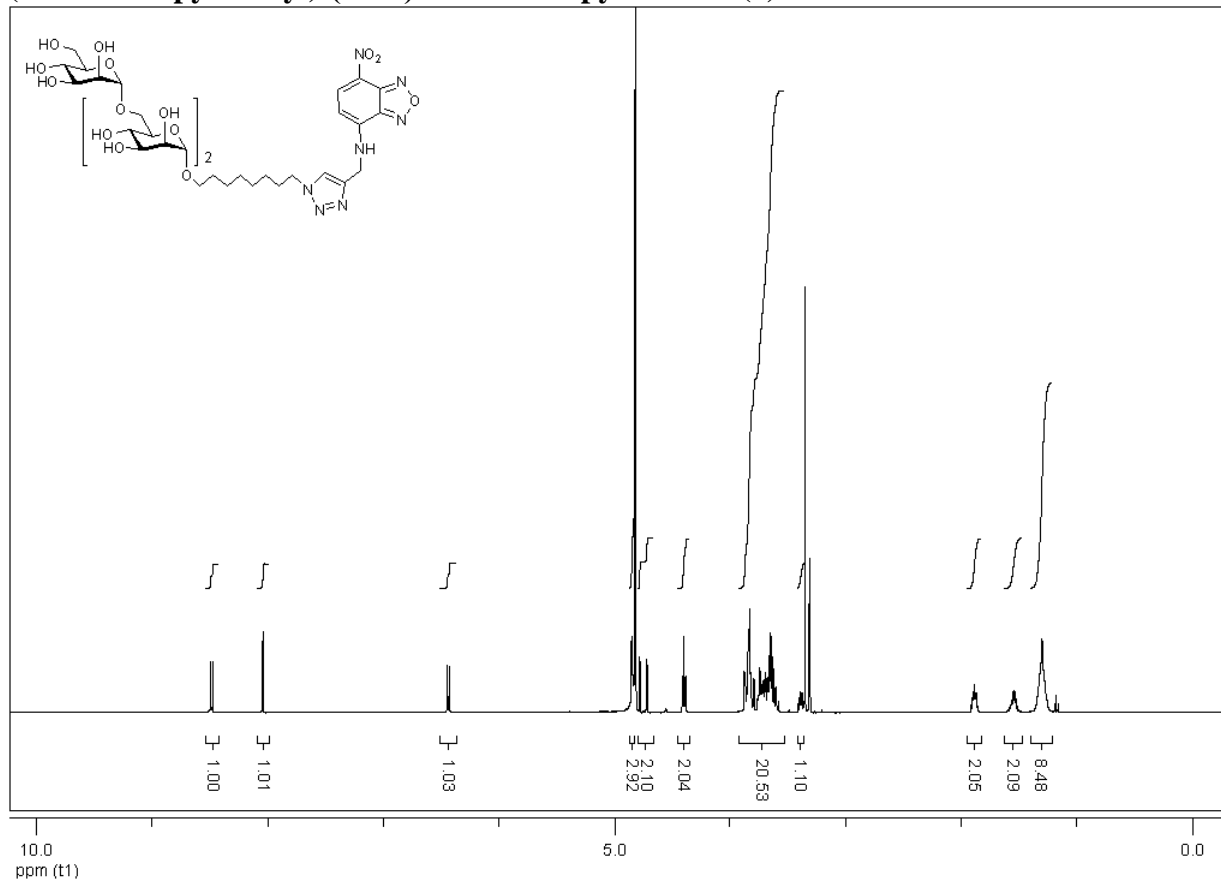
# Azidoethyl 2,6-di-O- $\alpha$ -D-mannopyranosyl- $\alpha$ -D-mannopyranoside (4)



**4-[(7-Nitrobenzofurazan-4-yl)aminomethyl]-triazol-1-yloctyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (5)**

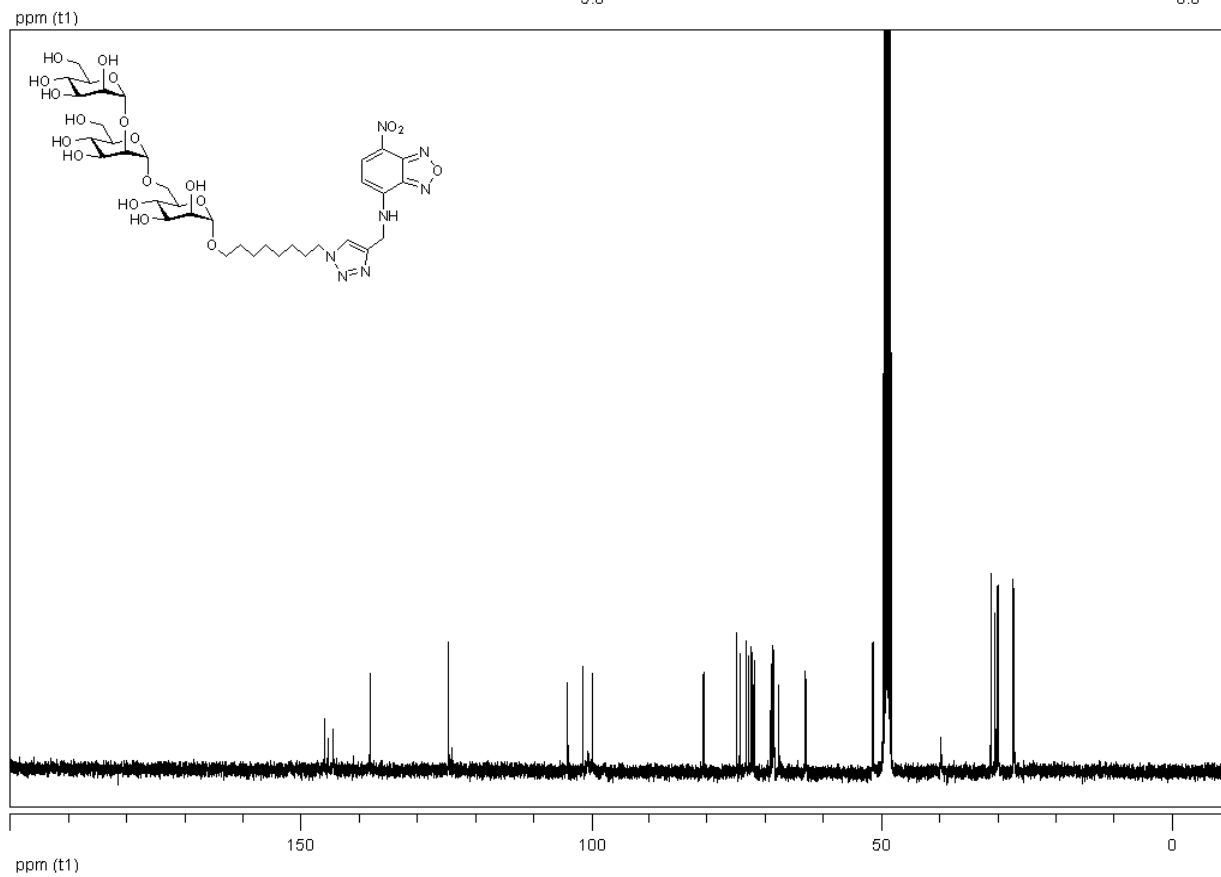
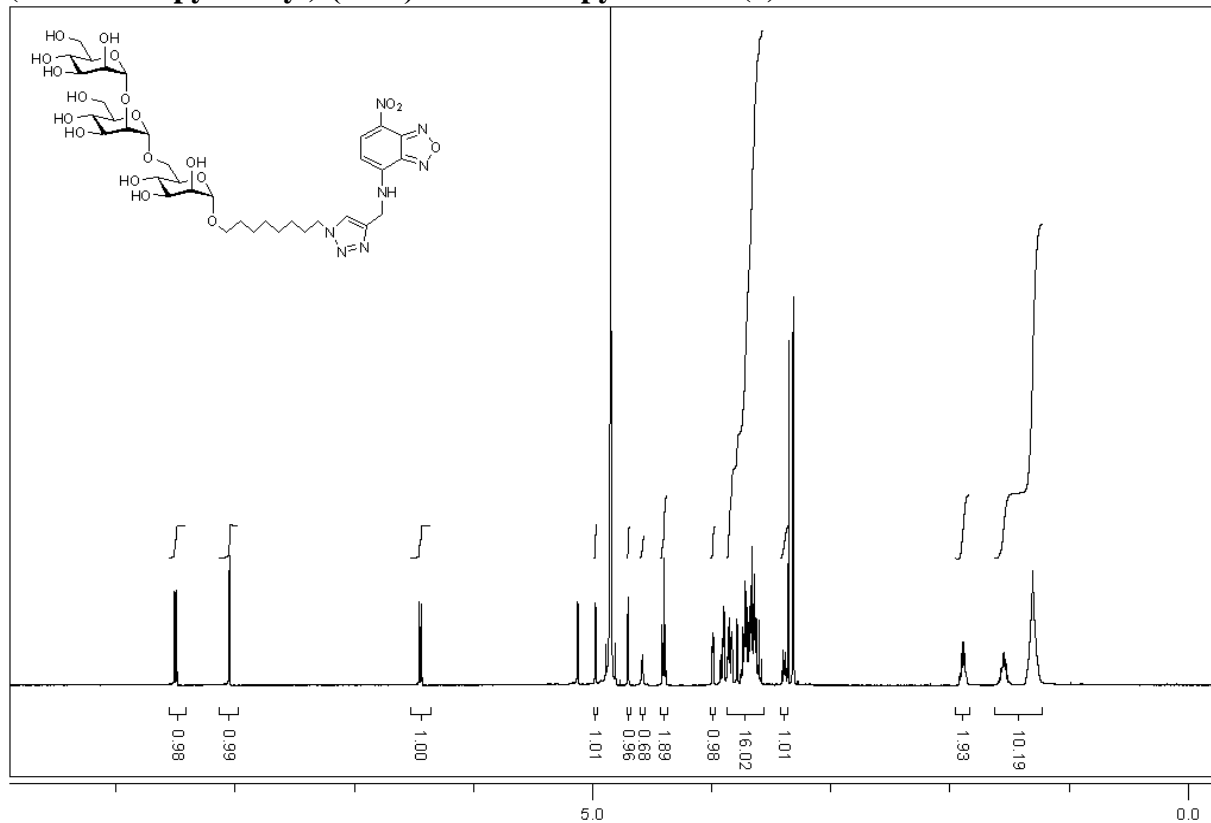


**4-[(7-Nitrobenzofurazan-4-yl)aminomethyl]-triazol-1-yloctyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (6)**

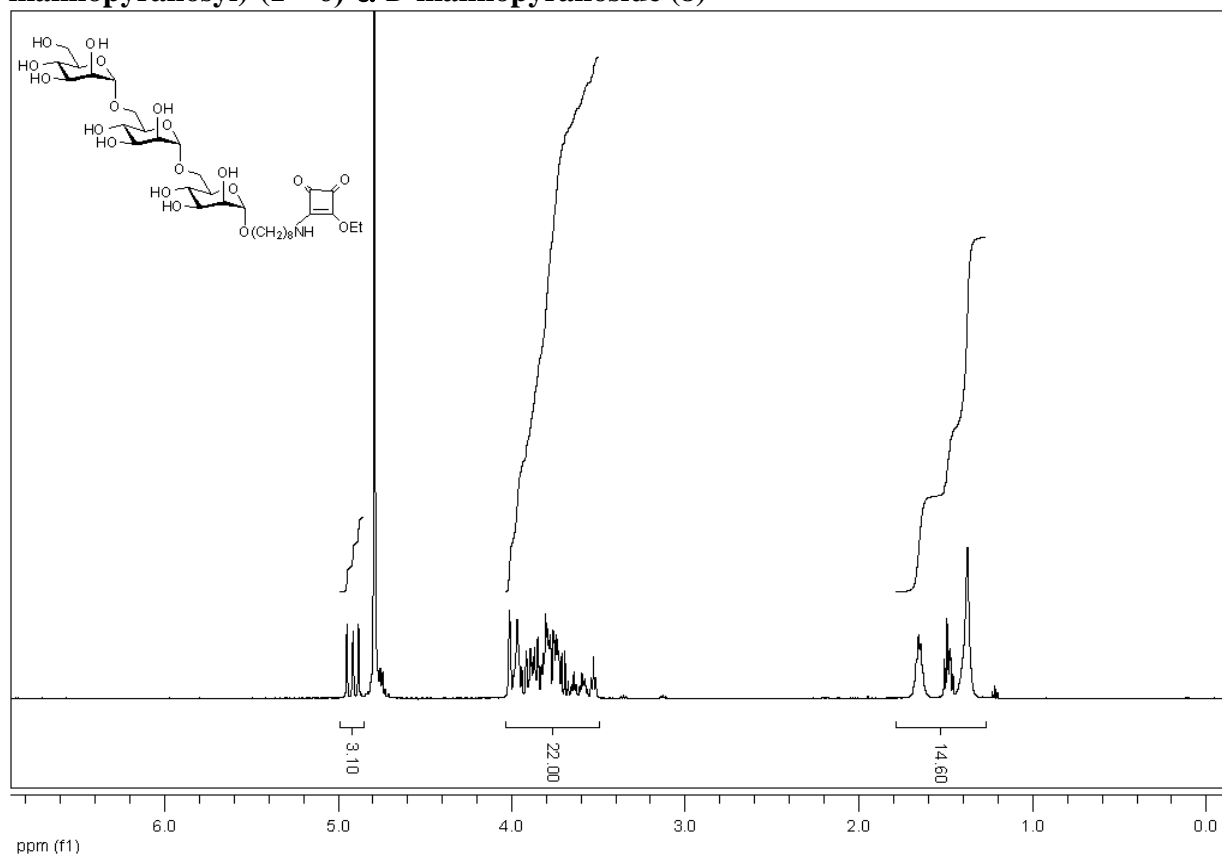




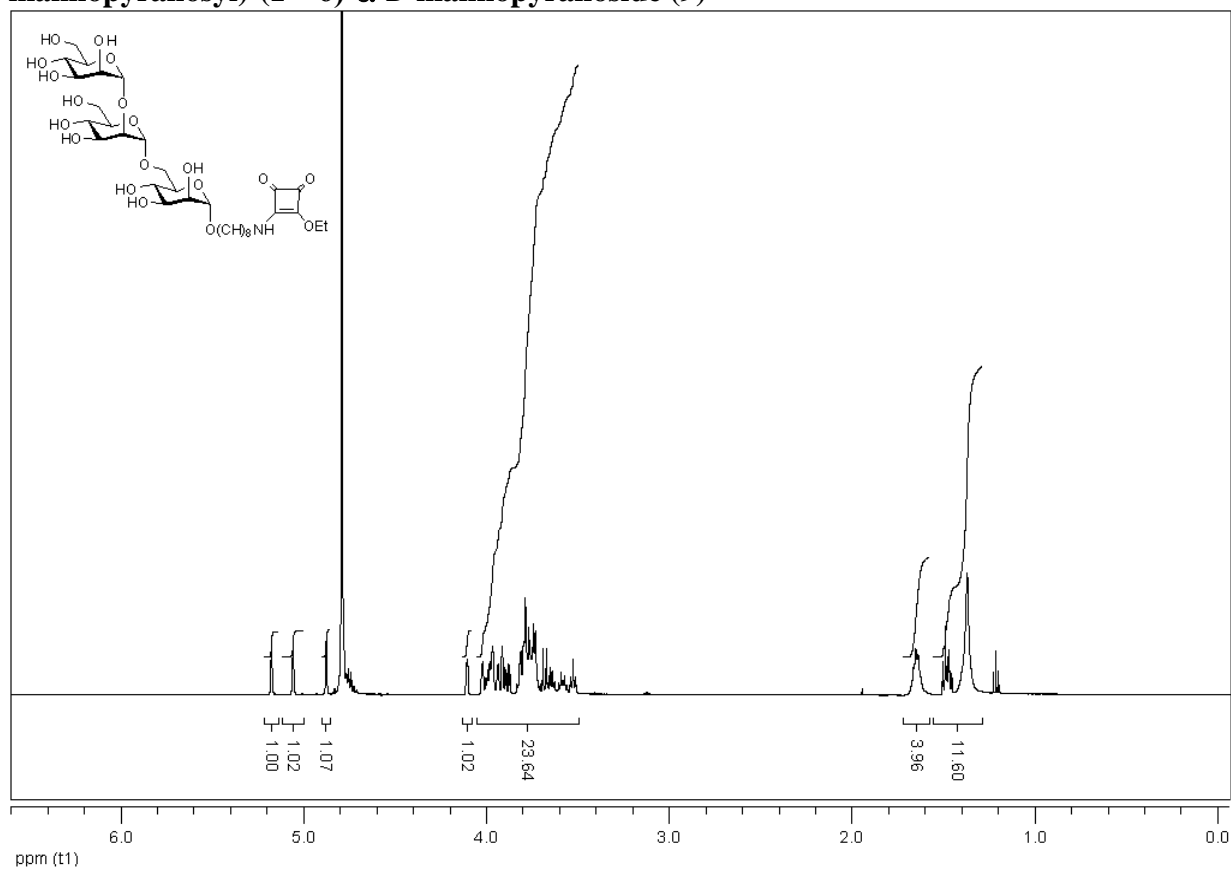
**4-[(7-Nitrobenzofurazan-4-yl)aminomethyl]-triazol-1-yl-octyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 2)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (7)**



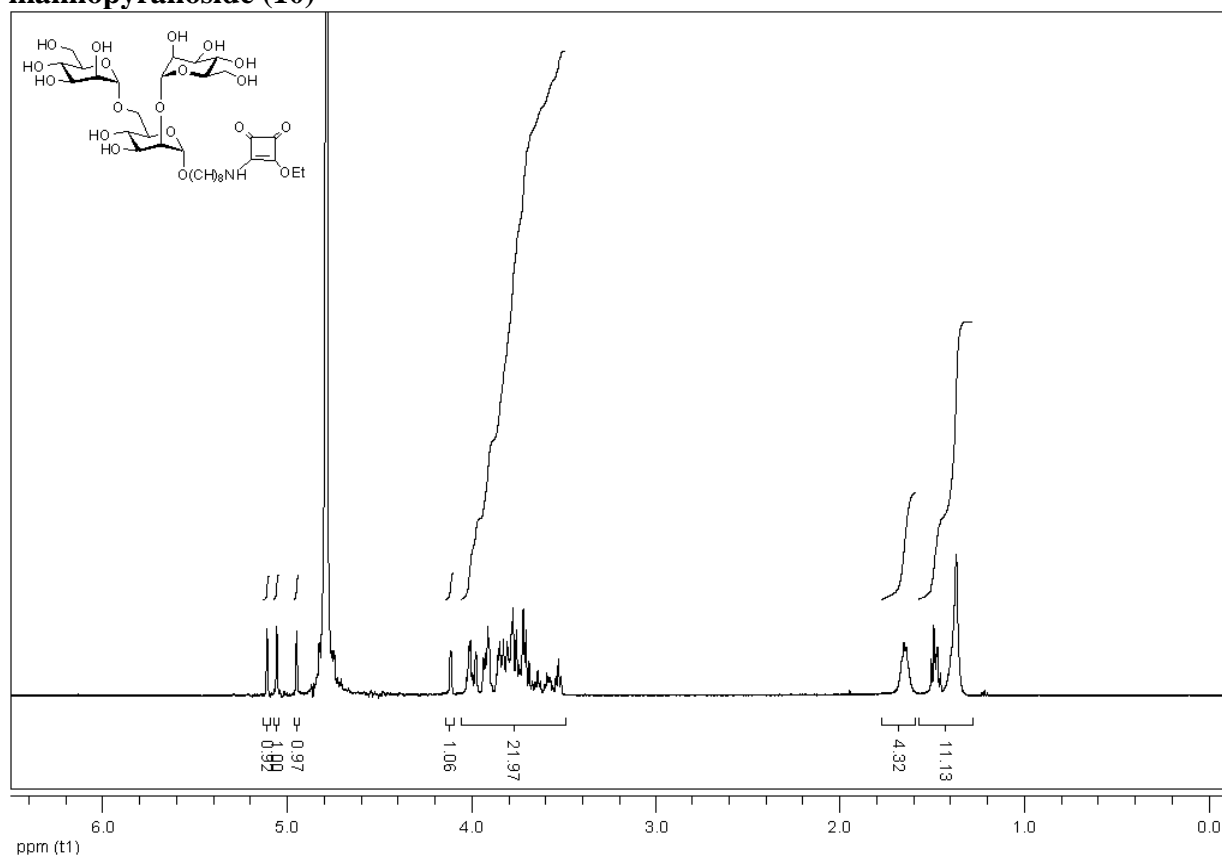
**8-(2-Ethoxycylobutene-3,4-dione-1-ylamino)octyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (8)**

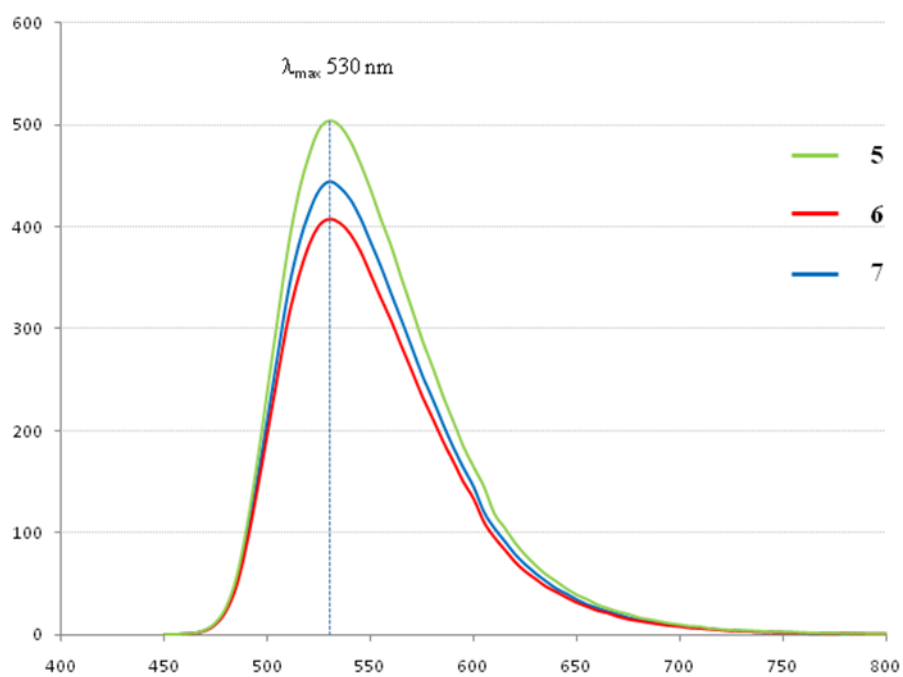


**8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl ( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 2)-( $\alpha$ -D-mannopyranosyl)-(1 $\rightarrow$ 6)- $\alpha$ -D-mannopyranoside (9)**



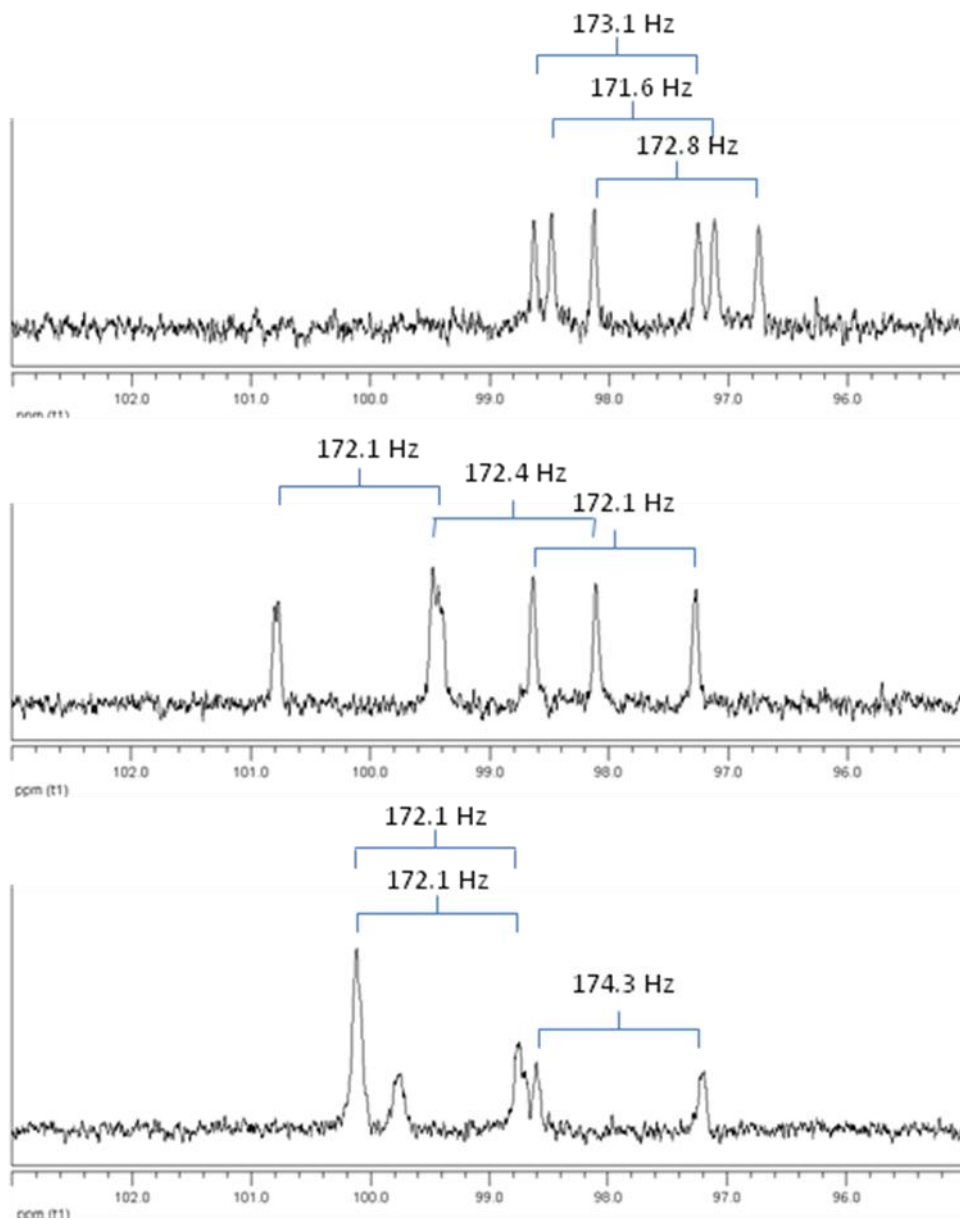
**8-(2-Ethoxycyclobutene-3,4-dione-1-ylamino)octyl 2,6-di-O- $\alpha$ -D-mannopyranosyl- $\alpha$ -D-mannopyranoside (10)**





**Figure 1:** Fluorescence emission spectra of the NBD-labelled neoglycoconjugates **5–7**.

$\lambda_{ex} = 400 \text{ nm}$  at  $0.1 \text{ mg ml}^{-1}$  in water.



**Figure 2:** 125 MHz  $^1\text{H}$  coupled  $^{13}\text{C}$  spectra of trisaccharides **25**, **28** and **29**.  $^1J_{\text{C,H}}$  values of anomeric carbons are indicated.