Supporting information for

Stereoselective synthesis of protected

3-amino-3,6-dideoxyaminosugars

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1. Structural studies

The relative configuration of azidopolyol **5** was secured through 1D and 2D NMR studies of isopropylidene acetal **15**. As shown in the next Figure, *anti*-C3,C5 relationship was supported by 13 C NMR whereas NOESY analyses confirm the 3,4-*syn*-4,5-*anti* configuration.



In turn, the configuration of pyranoses **8**, **18**, and **20** was established through 1D and 2D NMR studies. For instance, proton coupling constant pattern of deoxyaminosugar **8** is characteristic of a chairlike pyranose ring in which the C2 substituent is axial whereas the C3, C4, and C5 substituents are at the equatorial positions. This arrangement together with the analysis of diagnostic nOe interactions is consistent with the α anomer of a mannopyranoside sugar. Similar studies on **18** and **20** established that they had been obtained as 65:35 and 40:60 mixtures of α and β anomers respectively.



Furthermore, treatment of **20** with acetic anhydride afforded polyacetylated deoxyaminosugar **21** as a 40:60 mixture of diastereomers, whose ¹H and ¹³C NMR peaks for the major anomer matched to the data reported in the literature for the β -1,2,4-tri-*O*-acetyl-3-amino-*N*-benzyloxycarbonyl-3,6-dideoxyglucopyranose.¹

¹ H. Chen, H. Yamase, K. Murakami, C. Chang, L. Zhao, Z. Zhao, H. Liu, *Biochemistry* 2002, 41, 9165.

2. ¹H and ¹³C NMR spectra













































