

## Synthesis of β-D-mannopyranosyl derivatives from a novel 2,3;4,6-Di-O-isopropylidene-D-glucal

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Carbohydrates, as the electrophilic species in glycosylation reactions, are usually limited by the variability of aglycones that can be introduced into the sugar moiety. Therefore, glycals (1,2-unsaturated derivatives of carbohydrates) were designed to enable  $\alpha$ -metalation of their vinyl ether functionality. However, the application of these C-1 metalated glycals is complicated by the subsequent stereoselective hydroxylation of C-2 resulting in a fully hydroxylated glycosyl derivative. To avoid this step of oxidation, synthesis A-7 and C-1 metalation of 2,3:4,6-di-O-isopropylidene-D-glucal (1), as an innovative protected 2-hydroxyglycal, have been optimized. We have proved that this C-1 lithiated intermediate can be efficiently used for the high-yield introduction of various electrophiles under relatively mild conditions. Furthermore, we have also shown that the obtained C-1 substituted protected 2-hydroxyglycals 2 can be easily transformed into the most challenging  $\beta$ -D-mannopyranosyl derivatives 3 with exclusive  $\beta$ -stereoselectivity. Using the approach mentioned above, the synthesis of ADP-I-glycero- $\beta$ -d-manno-heptose analogue 4 as a potential inhibitor of bacterial heptosyltransferase was optimized.

Use of 2,3:4,6-di-O-isopropylidene-D-glucal (1).

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