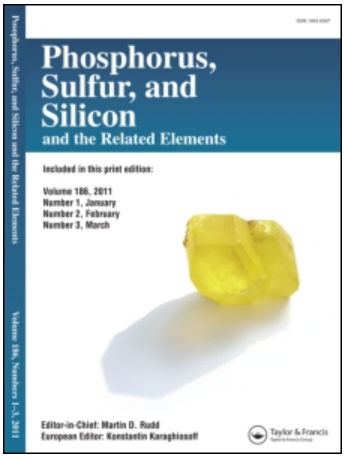

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Highly Diastereoselective Synthesis of Anomeric ß-O-Glycopyranosyl $\sigma^3\lambda^3$- and $\sigma^4\lambda^5$-Phosphorus Compounds

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A new method for the highly stereoselective synthesis of β-O-$\sigma^3\lambda^3$ and $\sigma^4\lambda^5$ phosphorus-substituted 2,3,4,6-tetrabenzylglucose is presented. The β-diastereoselective synthesis of the carbohydrates containing $\sigma^3\lambda^3$ and $\sigma^4\lambda^5$ phosphorus groups could be accomplished via two main synthetic routes. The first involves the addition of the $\sigma^3\lambda^3$-phosphorus derivative **3** to the 2,3,4,6-tetrabenzylglucose derivative **1** (α:β = 1:1) in toluene and triethylamine as a catalyst to provide the $\sigma^3\lambda^3$ phosphorus derivative **4** with practically 100% β-diastereoselectivity.

The second route involves the β-stereoselective formation of the $\sigma^3\lambda^3$- and $\sigma^4\lambda^5$-phosphorus-fluorine derivatives **7** and **8** by the reaction of the β-trimethylsilyl-glycoside **2** with $ClPF_2$ or $P(:O)F_3$ in the presence of PF_5 with loss of Me_3SiCl or Me_3SiF. The reaction of **2** with $P(:O)F_3$ in the absence of PF_5 did not lead to the expected product **8**. The use of **4**, **7**, **8** and other bis(2-chloroethyl)amino-substituted derivatives of phosphorus-containing carbohydrates as glycosyl donors in the glycosylation reaction is discussed.