Significance: Toshima and co-workers report a highly β-selective glycosylation of α-trichloroacetimidates with various secondary alcohols. The diastereoselectivity is moderate to excellent, and the reaction is mediated by the phosphoric acid \((S)-3\) at 60 mol%. According to mechanistic studies, the exclusive β-selectivities are obtained through a \((S)-3\)-mediated SN2 reaction pathway. The methodology was also applied to the total synthesis of a natural flavan glycoside using a racemic aglycone.

Comment: Glycosylation is an important synthetic method to construct sugar moiety containing compounds. Here, the authors report a novel Brønsted acid mediated glycosylation, and a kinetic resolution of secondary alcohols occurs during the process at the same time. This methodology provides a straightforward way for the synthesis of sugar-derived products with high stereoselectivity.