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Chiral Brønsted Acid Mediated Glycosylation with Recognition of Alcohol Chirality *Angew. Chem. Int. Ed.* **2013**, *52*, 12131–12134.

Phosphoric Acid Mediated Glycosylation and Alcohol-Chirality Recognition

Selected examples:

HO. HO. Ph 85% yield (β, R) 87% yield (β, R) 67% yield (β, R) 0% yield (β, S) 0% yield (β , S) 13% yield (β, S) OTBDPS OMe (\pm) (±) 84% yield (β, R) 75% yield (β, R) 77% yield (β, R) 17% yield (β, S) 0% yield (β, S) 8% yield (β, S)

Reaction pathway:

Significance: To shima and co-workers report a highly β -selective glycosylation of α -trichloroacetimidates $\mathbf{1}\alpha$ with various secondary alcohols. The diastereoselectivity is moderate to excellent, and the reaction is mediated by the phosphoric acid (S)-3. According to mechanistic studies, the exclusive β -selectivities are obtained through a (S)-3-mediated S_N2 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.

SYNFACTS Contributors: Benjamin List, Qinggang Wang Synfacts 2014, 10(1), 0091 Published online: 13.12.2013 **DOI:** 10.1055/s-0033-1340411; **Reg-No.:** B12413SF