SHELF-STABLE 3-THIOCRESYL-PROP-1-ENYL (TCP) GLYCOSIDES IN GLYCOSYLATIONS

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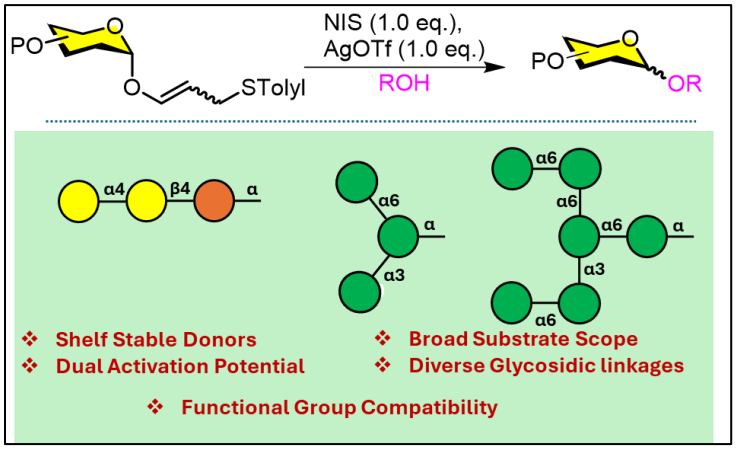
Well-known allyl glycoside activation in glycosylations involve transition metal-catalyzed isomerization to a glycosylation-active vinyl glycoside. In an effort to develop a shelf-stable, active vinyl glycoside, we present a method to transform a of latent allyl glycoside to the corresponding vinyl glycoside, as a TCP glycoside. The TCP glycoside is synthesized by allylic bromination of allyl glycoside, followed by reaction with sodium salt of thiocresol. The TCP glycosides are shelf-stable for more than a year. Utilizing *N*-iodosuccinimide / silver triflate reagents, a remote electrophilic activation occurs, leading to the formation of glycosylation-active intermediate, reaction of which with a glycosyl acceptor completes the glycosylation. The effectiveness of TCP glycoside donors in glycosylations is demonstrated through the synthesis of a number of di- to hhexasaccharides of varying constitutions, in pyranosides and furanosides, including the globo-trioside Gb3 antigen. The reactions also confirm the transformation of disarmed-TCP glycosides to armed-TCP glycosyl donors, illustrating the compatibility with protective group variations. The synthetic utility of TCP glycoside donors is validated through the synthesis of biologically relevant tri- and hexasaccharide oligomannans, establishing the potential of these new donors for oligosaccharide synthesis. Mechanistic studies indicate the remote activation of the thioether moiety by promoters, as evidenced by the identification of thioether and acrolein by-products.



Reference:
1. D. Kushwaha, A. Das, N. Jayaraman."Shelf-Stable 3-Thiocresyl-prop-1-enyl (TCP) Glycosides in Oligosaccharide Synthesis", *Chem. Eur. J.* **2025**, DOI: 10.1002/chem.202500372