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In this article, we disclose a useful and efficient synthetic method to derive thioglycosides of 2-deoxysugars. We have identified that the treatment of glycals with ceric ammonium nitrate in the presence of ethanethiol leads neatly to the formation of 2-deoxy-1-thioglycosides. A rather mild synthesis of 2-deoxy-1-thio sugars is also rationalized by a possible mechanism of their formation. Upon establishing the synthesis, we have tested further the efficiencies of the newly derived 2-deoxy-1-thio sugars in representative glycosylation reactions and are found to act as excellent glycosyl donors. Whilst, at present, there exists different methods for the formation of 2-deoxy glycosides, including those involving glycals, the method reported herein stands out, since an activated 2-deoxyglycosyl donor, namely, 2-deoxy-1-thioglycoside is produced. Such activated sugar derivatives should be very useful to glycosylate a variety of aglycosyl and glycosyl acceptors.