Site-selective photobromination of carbohydrates – synthesis and applications

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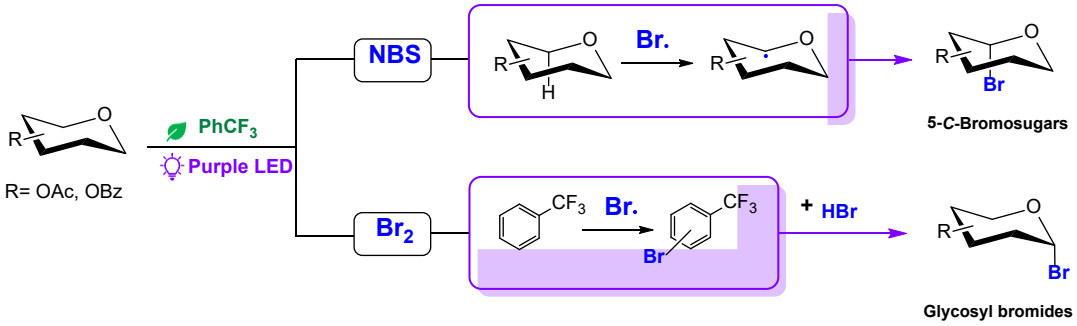
The Ferrier photobromination provides direct synthetic access to valuable 5-*C*-bromosugars.[1] However, its broader application has been constrained by the use of broad spectrum, energy-inefficient heat lamps for irradiation and a reliance on highly toxic (and banned) CCl_4 under reflux. Herein we demonstrate that the reaction proceeds rapidly and efficiently under mild conditions (≤40 °C) using benzotrifluoride ($PhCF_3$) as a safe and environmentally benign alternative to CCl_4, with irradiation by a compact photoreactor fitted with purple LEDs (405 nm), and NBS serving as the bromine source.[2,3]



Mild reaction conditions | Flow-photochemistry | Scalable | Up to 97% yield

Furthermore, we have now developed a simple, rapid and scalable photocatalytic method to prepare glycosyl bromides under mild conditions by substituting Br_2 for NBS as the brominating agent.[4] This reaction proceeds via generation of HBr *in situ* from radical bromination of $PhCF_3$ under purple light irradiation. This method is environmentally friendly, limiting the amount of HBr and waste generated, and we demonstrate its use to prepare glycosyl bromides in flow on a multigram scale. Recent results on new photochemical methods to convert these glycosyl bromides into anhydroalditols, 2-deoxysugars and *C*-glycosides will also be discussed.

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2. Zhang, G.; See, N. W.; … Furneaux, R. H.; Ferro, V. *Org. Lett*. **2024**, *26*, 5956–5960.
3. Zhang, G.; See, N. W.; … Furneaux, R. H.; Ferro, V. *J. Org. Chem.* **2025**, *90*, 16885-16890.
4. Zhang, G.; See, N. W.; Furneaux, R. H.; Ferro, V. *ChemRxiv*, **2026**, https://doi.org/10.26434/chemrxiv.15001901/v2