

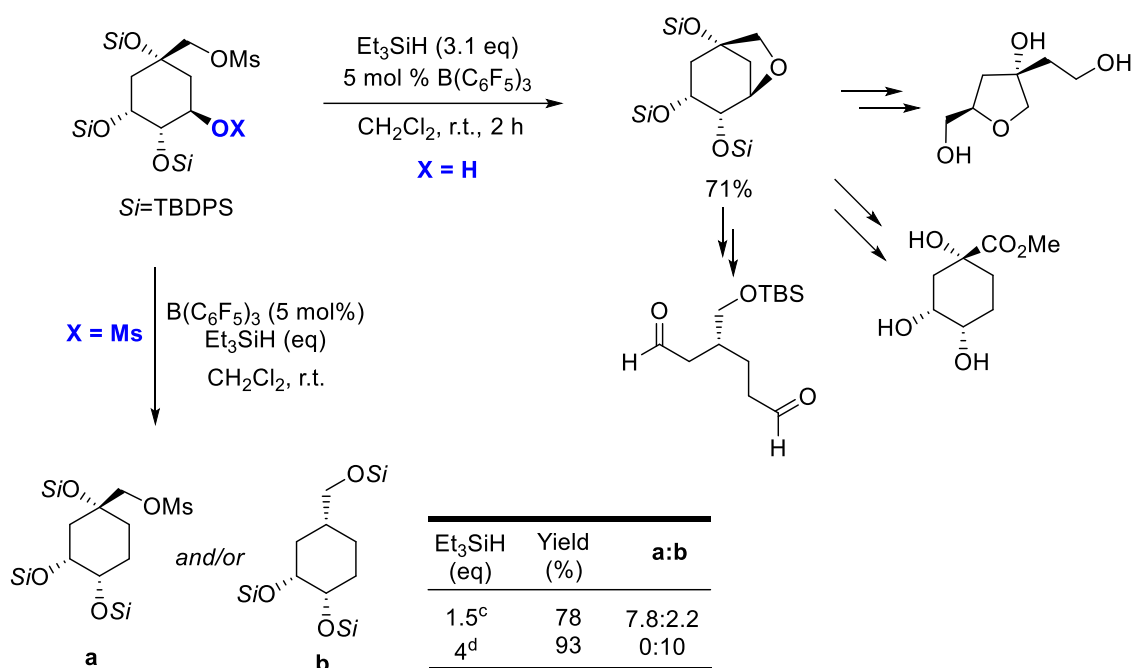
Quinic acid chirons by Stereoselective Borane-catalyzed Cleavage of C(sp³)-O Bonds

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The B(C₆F₅)₃-catalyzed reduction of C–O bonds with hydrosilanes has been rapidly expanding the accessibility to saccharides-derived chiral fragments for synthesis.[1] On the other hand, natural cyclitols have been scarcely considered as substrates in generating synthetic fragments derived from C–O cleavage of silylated derivatives. Herein we display our results on the selective cleavage of C(sp³)-O bonds of a common quinic acid-derived precursor. Quinic acid, a secondary metabolite of the shikimate pathway, has a three-dimensional arrangement of secondary hydroxy groups and methylene units that can greatly overlap with the functional groups to be adapted in the chiron strategy in total synthesis.[2]

The previously reported anchimeric assistance by silyl ethers in the C–O bond cleavage of sulfonates[3] was explored in the B(C₆F₅)₃-catalyzed defunctionalization of a quinic acid derivate, through hydride delivery to three-membered silyloxonium ions. The success of the deoxygenation protocol was deemed dependent on the protecting group, as the installation of the mesylate vicinal to silyl ether groups provided a system prone for the desired stereoselective C–O cleavage. The diversification of the reaction conditions allowed the construction of different defunctionalized fragments foreseen as useful synthetic fragments and had diversified the array of molecules and fragments that can be obtained from biorenewables.[4, 5]



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[4] Holmstedt, S.; George, L.; Koivuporras, A.; Valkonen, A.; Candeias, N. R., *Org. Lett.*, **2020**, 22, 8370.

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