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Stereoselective synthesis of a novel branched-chain (1*S*,2*R*,6*R*,7*S*)-7a-(hydroxymethyl)-1,2,6,7-tetrahydroxypyrrolizidine

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ABSTRACT

An efficient and highly stereoselective approach towards a new type of branched-chain pentahydroxylated pyrrolizidine **7** from a D-glucose isothiocyanate scaffold has been developed. The key features of this strategy are the construction of a diene-substrate foldamer possessing an amino functional group followed by subsequent ring-closing metathesis, an intramolecular cyclization readily induced by regioselective tosylation to establish the pyrrolizidine unit and a highly diastereoselective, substrate-controlled dihydroxylation.

Introduction

Polyhydroxylated pyrrolizidine alkaloids such as compounds **1-5** (Fig. 1), isolated from various plant families, represent an impressive structural motif that has proven to be a rich source of glycosidase inhibitors.¹ Although a number of members of this compound class have been studied at a clinical level, none of them have been approved as a drug. Attempts to improve the selectivity and efficiency of these inhibitors with minimal side effects have been made to develop several analogues of the naturally occurring heterocycles to meet the aforementioned challenges.² For most pyrrolizidines, the presence of the hydroxymethyl side chain at the C-3 position (*e.g.* casuarine **1**, uniflorine **2**, pochonicine **3**) or at the C-1 position (*e.g.* platinecine **4**, rosmarinecine **5**) is typical. On the other hand, only a few alkaloids

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