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Synthesis of Functionalized Tetrahydrofurans from Hydroxy Sulfinyl Dienes

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Hydroxy sulfinyl dienes yielded functionalized tetrahydrofurans through nucleophilic and metal-catalyzed epoxidations.¹ Effective oxirane cleavage has been achieved in these systems and a formal synthesis of (–)-Kumausallene is reported.

Keywords Asymmetric synthesis; epoxides; sulfoxides; tetrahydrofurans

INTRODUCTION

We report our recent results that have led to carbohydrate precursors and the development of efficient and stereoselective conditions to transform the oxirane moiety into ketones and alcohols. These conditions have been applied to the formal synthesis of a natural product.

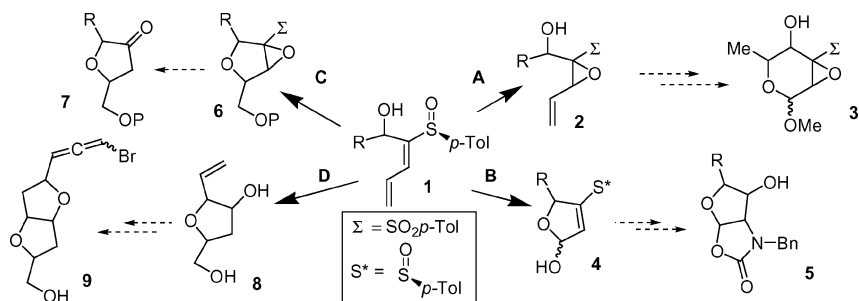
RESULTS AND DISCUSSION

Route **A** gave us an entry to carbohydrate precursors **3** *via* electrophilic epoxidation of hydroxy sulfinyl diene **1**. Route **B** led to tetrahydrofuro-oxazolones **5** through intramolecular Michael addition followed by Pummerer reaction. Using our methodology (route **C**), we could prepare configurationally stable ketones **7** by oxirane cleavage with MgI_2 applied to **6**. Synthesis of bromoallenes **9** (route **D**) represents a formal

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synthesis of (–)-Kumausallene, modifying key intermediate **8** during the process.

REFERENCE

- [1] R. Fernández de la Pradilla, P. Manzano, C. Montero, J. Priego, M. Martínez-Ripoll, and L. A. Martínez-Cruz, *J. Org. Chem.*, **68**, 7755–7767 (2003).