

# Accepted Manuscript

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## 5'-Spiro-cyclopropanated lactose derivatives as suitable intermediates for the chain elongation: synthesis of a new 6-deoxy-6-methyl $\delta$ -eptulose<sup>†</sup>

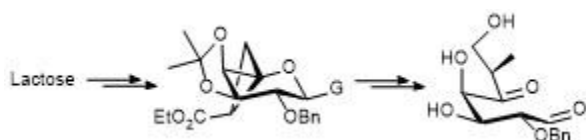
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### Highlights

- Higher-carbon sugars have a prominent role in biological processes.
- The chain extension by cyclopropanation has not been thoroughly explored.
- Hex-5'-enopyranoside was cyclopropanated with addition of ethoxycarbonyl carbene.
- The experimental results have been rationalized with computational calculations.

### Graphical Abstract



**Abstract:** A  $\delta$ -dicarbonyl heptose has been prepared through an electrophilic ring opening procedure of a 5'-spirocyclopropanated lactose derivative. The reported synthetic procedure outlines a new route for the transformation of this renewable disaccharide into new and interesting  $\delta$ -dicarbonyl sugars, synthetic precursors of cyclitols, carba- and azasugars. The experimental results of the cyclopropanation process, have been successful rationalized by *in silico* studies.

### 1. Introduction

Aldosuloses are a class of saccharide derivatives containing two carbonyl groups. Although poorly investigated, these interesting natural dicarbonyl monosaccharides<sup>1</sup> were proposed to be involved in the biosynthesis of cyclitols.<sup>2-4</sup> Aldosuloses are also useful synthetic intermediates for the preparation of high value-added compounds such as carbasugars (*epi*-gabosine A),<sup>5</sup> cyclitols (*epi*- and *D-chiro*-inositol),<sup>6-8</sup> iminosugars (1-deoxynojirimycin)<sup>9</sup> and azadisaccharides.<sup>10</sup>

A general approach to aldohexos-5-uloses was developed using as key reaction the epoxidation-methanolysis reaction of 4-deoxy-hex-4-eno-<sup>11-16</sup> or 6-deoxy-hex-5-enopyranosides.<sup>17, 18</sup> Within a project on the elaboration of 5,6-unsaturated pyranosides, in the last years, we have studied the

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