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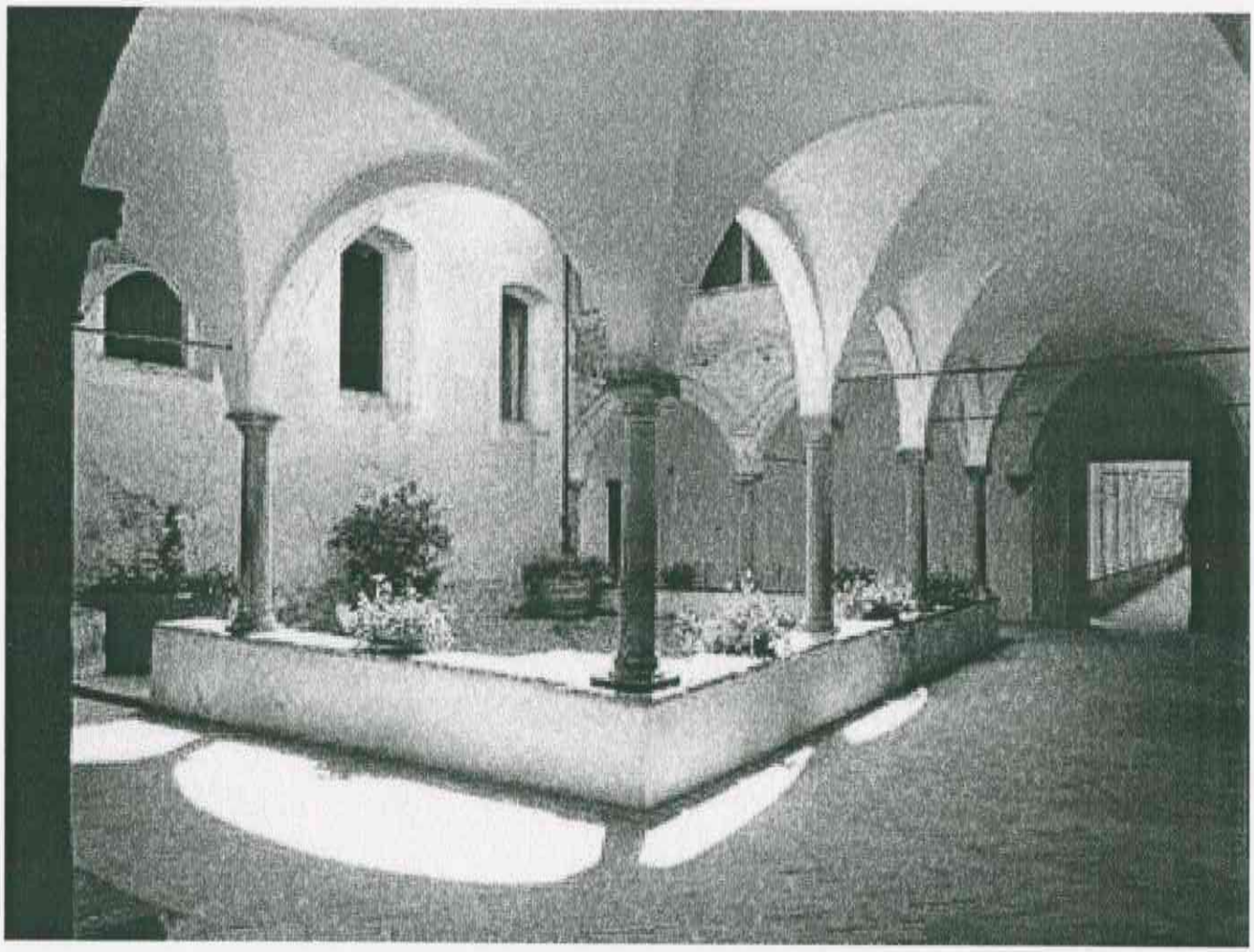

Università di Pisa
Dipartimento Scienze Farmaceutiche

Università degli Studi di Siena
Dipartimento Farmaco Chimico e Tecnologico

Università degli Studi di Firenze
Dipartimento Chimica "U. Shiff"

A 2,3-CARBAMATE-BEARING ALLYL GALACTOSAMINE DONOR FOR THE SYNTHESIS OF REPEATING α-(1→4)-LINKED GALACTOSAMINE UNITS

Maria Vetro,[a] Laura Legnani,[b] Lucio Toma,[b] Fiamma Ronchetti,[a] Federica Compostella[a]

[a] *Università di Milano, Dip. Chimica, Biochimica e Biotecnologie per la Medicina, via Saldini 50, 20133 Milano*
[b] Università di Pavia, Dip. Chimica, via Taramelli 10, 27100 Pavia

The 1,2-*cis*-linked 2-amino-2-deoxy sugar structure is found in various oligosaccharides of biological importance. The repeating Gal*p*NAc-α-(1→4)-Gal*p*NAc unit constitutes for example an essential motif incorporated in a range of oligosaccharides, e.g. the repeating unit of the O-antigen moiety of the lipopolysaccharide from *Escherichia Coli* O142 or *Sphaerotilus natans*.[1] Vi antigen is instead a linear homopolymer of α-(1→4)-linked N-acetyl galactosaminuronic monomers, with a variable degree of O-acetylation at the C3 position. Vi antigen is a capsular polysaccharide found mainly in *Salmonella typhi* and *Salmonella paratyphi C*, two serotypes of *Salmonella* that are responsible for severe infection in humans.[2]

Although in the past years there has been much progress in carbohydrate chemistry, 1,2-*cis*-selective glycosylation of gluco- or galactosamines is still a challenge. 2-Azidoglycosyl donors, developed many years ago, are still employed for the synthesis of 2-amino-2-deoxy α-glycosides, even if glycosylations suffer of low selectivity. Progress in resolving these issues has been made with the development of donors carrying a 2,3-*trans*-carbamate group, which has attracted much attention as a stereodirecting protection in glycosylation reactions. The fused carbamate ring proved to be a non-participating group and favors the formation of α-glycosides. So far, different studies have demonstrated that 2,3-oxazolidinone protected thioglycosides are highly efficient substrates for the synthesis of α-linked glycosides.[3]

Herein we report a new 2,3-oxazolidinone protected galactosamine donor, bearing an allyl group at the anomeric position. The allyl group, in addition to its traditional role as a valuable anomeric protecting group, can also be converted into a good leaving group for glycosylation. Thus, the allyl glycoside is first isomerized to the corresponding prop-1-enyl glycoside, which, after chemoselective activation of the anomeric enol ether moiety with a suitable electrophile in the presence of the glycosyl acceptor, leads to the formation of the disaccharide product.[4] This method has the advantage that prop-1-enyl glycoside can be directly derived from allyl glycoside with a variety of facile and highly effective isomerization methods and immediately subjected to glycosylation.

Herein we describe the synthesis of a galactosamine building block, which has the anomeric position protected by an allyl group, and positions 2 and 3 involved in the formation of an oxazolidinone ring. The proper donor and acceptor to perform a α-(1→4) glycosylation have been obtained from this common building block. The new 2,3-oxazolidinone protected allyl galactosamine donor has been subjected to glycosylation reactions to study its reactivity and the stereoselectivity of the process.

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3. See for examples: a) Kerns R.J., Zha C., Benakli K.,. Liang Y.Z, *Tetrahedron Lett.* **2003**, *44*, 8069; b) Olsson, J. D. M.; Eriksson, L.; Lahmann, M.; Oscarson, S. *J. Org. Chem*: **2008**, *73*, 7181; c) Yang, L.; Ye, X-S. *Carbohydr. Res.* **2010**, *345*, 1713; d) Yang, L.; Zhu, J. ; Zheng, X-J. ; Tai, G. ; Ye, X-S. *Chem. Eur. J.* **2011**, *17*, 14518
4. Wang, Y.; Zhang, X.; Wang, P. *Org. Biomol. Chem.* **2010**, *8*, 4322 and references herein reported.

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