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Total synthesis of alginate and zwitterionic SP1 oligosaccharides

Zhang, Q.

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Author: Zhang, Q.

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Stellingen
behorende bij het proefschrift
Total Synthesis of Alginate and Zwitterionic SP1 Oligosaccharides

1. Further variation of the leaving groups will probably not lead to major improvement of the existing methodologies for glycoside bond formation. Rather, a deeper understanding of underlying mechanistic principles (ion-pair generation, memory effects of tight ion pairs, conformation-dependent reactivity, stereodifferentiation of the glycosyl donor between nucleophiles, and other factors) will lead to further advances.

X. Zhu and R. R. Schmidt, *Angew. Chem. Int. Ed.* 2009, 48, 1900-1934.

2. Although the leaving group could determine the donor stability and promotion conditions, the final outcome of a glycosylation reaction is a result of the interplay of many elements. The efforts to search for a 'better' glycosylation reaction will not stop until non-specialists are able to make the glycosidic linkages in a manual way.

J. Sun and B. Yu, *Chem. Commun.*, 2010, 46, 4668-4679.

3. The use of conformationally flexible building blocks can be an effective approach to overcome steric interactions in the crowded transition state of a glycosylation reaction, by allowing the acceptor to adopt a sterically most favourable shape.

This thesis, Chapter 4.

4. The use of the simple "toolset" of partially fluorinated ethanols represents a rapid and easy means to investigate glycosylation reaction mechanisms and report on the robustness of glycosylation protocols.

S. van der Vorm, T. Hansen, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, *Chem. Sci.*, 2017, 8, 1867-1875.

5. Our growing insight into the mechanisms of glycosylation reactions in combination with the future availability of commercial synthesizers and ever more powerful purification techniques will open up new avenues in glycochemistry and glycobiology.

M. T. C. Walvoort, H. van den Elst, O. J. Plante, L. Kröck, P. H. Seeberger, H. S. Overkleeft, G. A. van der Marel, J. D. C. Codée, *Angew. Chem. Int. Ed. Engl.* 2012, 51, 4393-4396.

6. Zwitterionic polysaccharides are T-cell dependent antigens as they can be processed by antigen presenting cells, loaded onto MHC II molecules and presented to T-cells, and thus are able to elicit an immune response.

B. A. Cobb, Q. Wang, A. O. Tzianabos, D. L. Kasper, *Cell*, 2004, 117, 677-687.

7. The development of CPS-based vaccines and the design of glycoconjugate vaccines were milestones in the prevention of bacterial infections. Current research deals with the development of carbohydrate-based vaccines against further diseases such as cancer or infections caused by viruses, fungi, protozoan parasites, and helminths.

J. Hütter and Bernd Lepenies (ed.), *Carbohydrate-Based Vaccines: Methods and Protocols*, Methods in Molecular Biology, vol. 1331, DOI 10.1007/978-1-4939-2874-3_1, © Springer Science+Business Media New York 2015.

8. **No pains no gains** (一份耕耘一份收获).

Leiden, 6 september 2018

Qingju Zhang