

PREFACE

For over a century, much progress in glycochemistry accumulated over the foundations laid upon by that scientific edifice, Emil Fischer. Since then, our understanding has certainly grown, and our techniques have steadily advanced in great proportions. The realization that glycans are important players in biological systems beyond their traditional roles as energy sources and structural support molecules instilled an astonishing amount of interest in defining their functions. Glycans are now known to impart widespread influence over important biological processes from fertilization to development to cancer progression and from bacterial and viral infection to immune response. Not surprisingly, they have become inspirations for the design of several pharmaceuticals and vaccines.

That sugars carry dense structural information, by virtue of the multiple chiral centers and the numerous ways the glycosidic bond can be formed, has been deemed critical in many recognition, adhesion, and signal transduction events. Another aspect has, however, kept studies at bay: glycan formation is not directly template driven, leading to an abundance of glycoforms that made isolation of homogeneous materials such an arduous procedure. Thus, the synthesis of sugars in their many forms and sizes became a necessary prerequisite of structure–activity relationship evaluations as well as in the pursuit of pharmaceutical and industrial applications.

The rapid explosion of techniques, especially in the last few decades, provided carbohydrate chemists of today with many tools in their disposal to form their desired glycan structures. Still, the main challenge remains to be the efficient assembly of glycans in a regioselective and stereoselective manner. As described in this book, the reliance on conformational effects, anomeric effect, solvent effect, neighboring group participation, and more recent techniques such as intramolecular aglycone delivery have proven valuable in effective glycosidic bond formation. Within this

framework, novel synthetic designs were developed to form the sugar backbones in solution in a single vessel, by automation in solid phase, or in microfluidic environments and with enzymatic transformations as an aid to assembly and backbone modifications. These strategies have been applied to address the complex combinations of the nine common monosaccharide building blocks found in mammalian cells apart from the unusual ones displayed by other organisms. The available tools that pushed glycochemistry to remarkable heights enabled the preparation of glycoconjugates, hybrid carbohydrate-protein vaccines, multivalent sugar assemblies, glycan arrays, and many others.

This book covers the fundamentals and the exciting developments in the fields around glycochemical synthesis. It could serve as a concise resource material about the methods and approaches toward creating glycan structures and its conjugates. Glycochemical synthesis is loosely divided into strategies and applications in this book. Starting from the basic aspects of glycochemistry, the volume expands into specific solutions to challenges unique to oligosaccharide assembly, particularly in protecting group selection and regioselective and stereoselective glycosylations. Clever strategies to the synthesis of sugars, techniques in the preparation of (neo) glycoconjugates, and the contributions of carbohydrate synthesis to understanding structure-activity relationships and drug development are highlighted. All 19 chapters are written by experts and are meant to convey the knowledge and expertise that have made glycochemistry quite an exciting field of study. Selected illustrative examples are described all throughout the book to guide the readers in understanding the concepts and strategies. Citations to primary literature are provided. While we acknowledge that this book may not include every notable strategy and application related to glycochemical synthesis, we offer with confidence a very useful reference for advanced undergraduate and graduate students with keen interests in glycochemistry and for academic and industrial scientists focused on carbohydrate research.

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