

## DESCRIPTION FOR THE GENERAL PUBLIC

Although it is often claimed that any organic compound can be made, the practical availability of a potential target is an important factor in drug and new materials design. A novel synthetic methodology has the potential of opening up new paths to products with high added value and therefore is of great value to biological and medical research. As one of such ground breaking approaches, medium and large size ring formation reactions have broadly impacted on the methods used in material and medicinal chemistry and, consequently, in the pharmaceutical industry.

Compounds containing medium-sized (8 to 12 membered) and larger rings are found in a variety of natural products, pharmaceuticals and functionalized materials. Their prevalence in nature is proposed to be a result of the macrocyclic core providing a beneficial and delicate balance between conformational rigidity and flexibility, which allows for optimal binding to biological targets. Their unique features provide a basis for the wide variety of biological activities exhibited by these natural products, including antitumor, antibiotic and antifungal properties. Moreover, compounds containing medium-sized rings have been adapted as building blocks for various functional materials, such as hydrogels, functional supramolecular polymers, transmembrane channels, analytic sensors and drug delivery systems.

Nevertheless, their synthesis and application in drug development material chemistry continues to be a challenge owing to the complex nature of this structural class. Most of the reported methods of medium- and large-sized rings construction require relatively dilute conditions (lower than 0.05 M), using molar amounts of activation agents, or special precautions (dropwise addition of substrate) to suppress unwanted intermolecular reactions. All this adds up to a low yield of most cyclization processes, making them less practical than desired. Construction of a carbocyclic skeleton using simple operations and non-high dilution conditions is not a trivial issue, and there is a strong demand for the development of a new effective method.

Herein we propose a solution for this needs by providing the concise, flexible, green, and user friendly method of construction of structurally diverse medium- to large-sized carbo- and heterocycles *via* thermal or photochemical transformations of readily available, stable and safe to use 1,2,4,5-tetraoxanes and related compounds derived from cyclic ketones. Our ambition is to establish a reliable methodology that will allow for conversion of readily available organic molecules into useful, inaccessible by conventional means, medium- and large-size rings. We hope that the simplicity of proposed process will put this artful transformation in the ranks of the most useful methods of direct construction of complex macrocycles.

We believe that presented innovative solutions will broaden significantly the current state of the art of the synthesis of structurally diverse, medium and large carbo- and heterocyclic rings, expanding its scope and providing the research community with a very useful tool for macrocycles formation. As many areas of this field are still undiscovered, we will be able to deeply explore exciting empty spots of macrocyclic chemistry.