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Swiss Science Concentrates

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Short Abstracts of Interesting Recent Publications of Swiss Origin

Spectroscopic and Computational Studies on the Rearrangement of Ionized [1.1.1]Propellane and Some of its Valence Isomers: The Key Role of Vibronic Coupling

B. Müller, T. Bally*, R. Pappas, and F. Williams *J. Am. Chem. Soc.* **2010**, *132*, 14649

Universities of Fribourg and Tennessee (USA)

[1.1.1]Propellane, 1, which possesses one of the highest strain energies per C–C bound of all known cycloalkanes, is remarkably stable towards thermal decomposition. In contrast, the corresponding radical cation undergoes spontaneous consecutive cleavage of *three* lateral C–C bonds to yield the dimethyleneallene radical cation, 3. Surprisingly, the weak central bond of 1 remains intact and even becomes a double bond in the product. The pivotal role of vibronic coupling in determining the course of the rearrangements of 1 is highlighted.

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Efficient Ring-Closing Metathesis of Alkenyl Bromides: The Importance of Protecting the Catalyst during the Olefin Approach

M. Gatti, E. Drinkel, L. Wu, I. Pusterla, F. Gaggia, and R. Dorta* *J. Am. Chem. Soc.* **2010**, *132*, 15179

University of Zurich

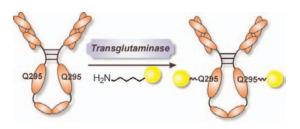
The authors report on the development of a catalytic method that enables access to cyclic alkenyl bromides *via* ruthenium-catalyzed ring closing metathesis. Efficient catalysis employing commercially available Grubbs II catalyst is possible through steric protection of the starting bromoalkene moiety. The starting diene compounds are easily accessible and should make this protocol attractive as a methodology for the construction of more elaborate molecular structures.

Site-Specific and Stoichiometric Modification of Antibodies by Bacterial Transglutaminase

S. Jeger, K. Zimmermann, A. Blanc, J. Grünberg, M. Honer, P. Hunziker, H. Struthers, and R. Schibli* *Angew. Chem. Int. Ed.* **2010**, *49*, 9995

ETH Zürich and Paul Scherrer Institute, Villigen

Novel, orthogonal, highly selective, and efficient conjugation reactions between small molecules and proteins are much sought after in order to enhance the toolbox that allows preparing, *e.g.* antibody conjugates for therapeutic applications. The authors report the modification of antibodies using a transglutaminase with a wide variety of amine-bearing substrates. These enzymes catalyze the reaction with glutamine residues in a specific, flexible region of the Fc region of antibodies, resulting in conjugates with superior *in vivo* characteristics.



Chiral N-Heterocyclic Carbene-Catalyzed Generation of Ester Enolate Equivalents from α , β -Unsaturated Aldehydes for Enantioselective Diels-Alder Reactions

J. Kaeobamrung, M.C. Kozlowski, and J. W. Bode* *Proc. Nat. Acad. Sci.* **2010**, *30*, 20661

ETH Zürich

The authors report the catalytic generation of chiral ester enolate equivalents from α,β -unsaturated aldehydes with a chiral *N*-heterocyclic carbene catalyst. These enolates can be used in highly enantioselective hetero-Diels-Alder reactions with electron-deficient enones. These reactions proceed under mild conditions and afford synthetically valuable products in excellent yield with outstanding stereoselectivities using a single catalyst precursor.