Silicon cation catalyzed (3+2)-Cycloadditions:

A joint Experimental and Computational Study

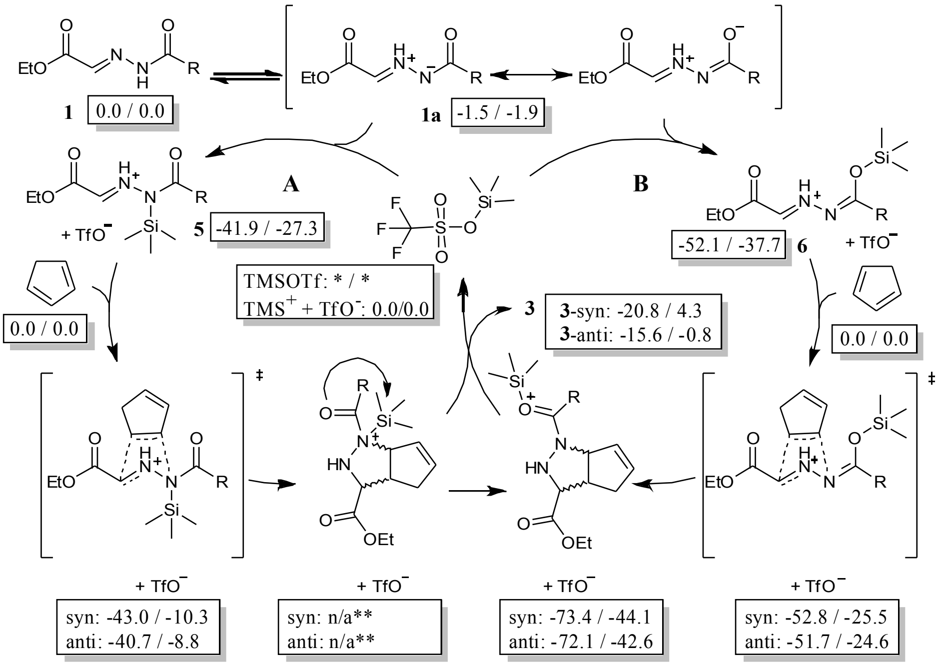
Sebastian Schenker,[a,b] Alexandru Zamfir,[a] Timothy Clark[b]
and Svetlana B. Tsogoeva[a]

[a]*Lehrstuhl für Organische Chemie I, FAU Erlangen , Henkestr. 42, 91054 Erlangen*

[b]*Computer Chemie Centrum, FAU Erlangen, Nägelsbachstr. 25, 91054 Erlangen*

A first and fairly mild metal-free catalytic route was developed for the (3+2)-cycloadditions of different N-acylhydrazones to cyclopentadiene, providing synthetically and biologically important five-membered cyclic compounds, pyrazolidines. The reaction has been successfully conducted in high yields (up to 99 %) with high diastereoselectivities (up to 98:2 *dr*) using catalytic amounts of TMSOTf (trimethylsilyl triflate) as readily available Lewis acidic catalyst.

Based on the experimental findings a density functional theory (DFT) study of the reaction mechanism was carried out at the B3LYP/TZV level of theory. For our reaction we find a mechanism via four-coordinate cationic silicon species. Lewis acidic activation of the hydrazone systems seems to be possible at different sites, yet an activation via the oxygen is preferred over an activation via nitrogen.



The theoretical and experimental diastereomeric excess values show good agreement, rendering the computations an efficient tool for quantitatively predicting the selectivities in these and related reactions.

Furthermore, we were able to locate several tuning possibilities for the development of new catalysts with increased activity, as well as enantioselective variants of these reactions.

[1] A. Zamfir, S. Schenker, W. Bauer, T. Clark, S. B. Tsogoeva,
Eur. J. Org. Chem. **2011**, *in press,* DOI: 10.1002/ejoc.201100206.