

BASIC INFORMATION ON SUB-PROJECT

NAME OF PROGRAMME/FUND	Scholarship Fund - Sciex NMS ^{ch}
RESEARCH FIELD AND OTHER RESEARCH FIELDS INVOLVED (if applicable)	Mathematics / Natural Sciences
TITLE OF THE SUB-PROJECT	Mechanism of the Photoactivated Uncaging of Nitrobenzyl-bound Reactants (NIBEMECH)
REGION OF THE CZECH REPUBLIC (according to the location of the home institution)	South Moravian Region
GRANT AMOUNT SPENT	35 347,45 CHF
INTERMEDIATE BODY	Swissuniversities
HOME INSTITUTION	Masaryk University Department of Chemistry
HOST INSTITUTION	University of Fribourg Department of Chemistry
NAME OF THE FELLOW	Tomáš Šolomek

ABSTRACT OF THE SUB-PROJECT

The project concerns the mechanism of the light-induced release of species that are "caged" by being bound to a nitrobenzyl photoremovable group, and the role of the photoinduced hydrogen atom transfer in the reaction sequence. Following laser flash photolysis experiments to follow the kinetics and the quantum yields for formation of the primary aci-nitro intermediates (to be carried out in Brno), the dependence of the quantum yields of the release of the benzylic substituents or H/D isotopes will be explained by performing quantum chemical calculations mapping the potential energy surfaces in the triplet or excited singlet manifold of states. Matrix isolation experiments will be performed on newly synthesized candidates for photodeprotection to reveal a possible participation of quantum mechanical tunneling, indirectly by phosphorescence measurements or directly by constructing the respective Arrhenius plots by coupled laser flash photolysis and low temperature argon matrix experiments. A complete picture of the entire mechanism will be created. Proposal of new improved and more efficient photoremovable groups based on the nitrobenzyl moiety will prosper from the knowledge attained in the present study.

<p>MAIN RESULTS</p>	<p>Within the scope of the SCIEX project: Šolomek T., Mercier S., Bally T., Bochet C. G. <i>“Photolysis of ortho-Nitrobenzylic Derivatives: The Importance of the Leaving Group” Photochem. Photobiol. Sci.</i> 2012, <i>11</i>, 548—555.</p> <p>Beyond the scope of the project: Nunes C. M., Reva I., Pinho e Melo T. M. V. D., Fausto R., Šolomek T., Bally T. <i>“The Pyrolysis of Isoxazole Revisited: A New Primary Product and the Pivotal Role of the Vinylnitrene. A Low-Temperature Matrix Isolation and Computational Study” J. Am. Chem. Soc.</i> 2011, <i>133</i>, 18911—18923.</p> <p>Continuation of the collaboration after the SCIEX program:</p> <p>Šolomek T., Bochet C. G., Bally T. <i>“The Primary Steps in Excited State Hydrogen Transfer: The Phototautomerization of o-Nitrobenzyl Derivatives” Chem. Eur. J.</i> 2014, <i>20</i>, 8062—8067.</p> <p>Storz C., Badoux M., Hauke C. M., Šolomek T., Kühnle A., Bally T., Kilbinger A. F. M. <i>“One-Pot Synthesis and AFM Imaging of a Triangular Aramide Macrocyclic” J. Am. Chem. Soc.</i> 2014, <i>136</i>, 12832—12835.</p>
<p>DATE OF REALISATION OF THE FELLOWSHIP</p>	<p>1.4.2011 - 31.10.2011</p>
<p>MORE INFORMATION ON THE PROGRAMME</p>	<p>www.sciex.ch</p>