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VABILO NA PREGLOV KOLOKVIJ / INVITATION TO THE PREGL COLLOQUIUM

## **Dr. Dominique Cahard**

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## Četrtek, Thursday, 5. 6. 2014, ob / at 13h

Velika predavalnica Kemijskega inštituta / Lecture Hall at the National Institute of Chemistry; Hajdrihova 19, Ljubljana

## Enantioselective Metal-Catalyzed Hydrogen Transfer Reactions for the Construction of CF<sub>3</sub>-bearing Stereogenic Carbons

The synthesis of enantiopure molecules featuring a trifluoromethyl motif at a stereogenic carbon centre increasingly stimulates high interest in many laboratories. Such compounds can be approached by direct introduction of the CF<sub>3</sub> group or by exploitation of prochiral trifluoromethylated substrates.<sup>[1]</sup> The stereoselective construction of all-C tertiary CF<sub>3</sub>-bearing stereogenic carbon centres without any heteroatom substituent undoubtedly belongs to the most fundamental topics in fluorine chemistry and remains highly challenging. As tool for this purpose, we have investigated the ruthenium catalyzed redox isomerization of trifluoromethylated allylic alcohols to access enantioenriched  $\beta$ -trifluoromethyl carbonyl compounds. The catalytic redox isomerization is an efficient, selective, atom-economic, one-step process for isomerization of C=C bond of *O-allylic* substrates into saturated carbonyl compounds.<sup>[2]</sup> In this method, a transition metal assists the migration of the carbon-carbon double bond into an enol which tautomerizes to the carbonyl compound. It is a conceptually attractive approach, which compares favorably with the more conventional sequential two-step oxidation and reduction reactions. Several issues were addressed during the search for optimal reaction conditions and will be detailed in the lecture. It includes (a) the choice of the catalyst, (b) the impact of the highly electron-withdrawing CF<sub>3</sub> group: electronic, steric, and position effects, (c) the gain of mechanistic insights, and (d) the stereocontrol of the newly created stereogenic centre.<sup>[3]</sup>

[1] (a) J.-A. Ma, D. Cahard, *Chem. Rev.* **2008**, *108*, PR1–PR43. (b) J. Nie, H.-C. Guo, D. Cahard, J.-A. Ma, *Chem. Rev.* **2011**, *111*, 455–529.

[2] (a) R. Uma, C. Crévisy, R. Grée, Chem. Rev. 2003, 103, 27–51. (b) L. Mantilli, C. Mazet, Chem. Lett. 2011, 40, 341–344.

[3] (a) V. Bizet, X. Pannecoucke, J.L. Renaud, D. Cahard, *Angew. Chem. Int. Ed.* **2012**, *51*, 6467–6470. (b) D. Cahard, V. Bizet, X. Dai, S. Gaillard, J.L. Renaud, *J. Fluorine Chem.* **2013**, *155*, 78–82. (c) V. Bizet, X. Pannecoucke, J.L. Renaud, D. Cahard, *Adv. Synth. Catal.* **2014**, *355*, 1394–1402.

## Vljudno vabljeni! / Kindly invited!

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