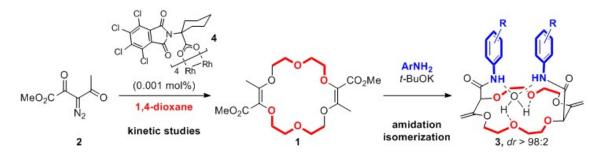
Kinetics of Rh(II)-Catalyzed α-Diazo-β-Ketoester Decomposition for Polyether Macrocycle Synthesis and Straightforward Access to Ditopic Cryptands

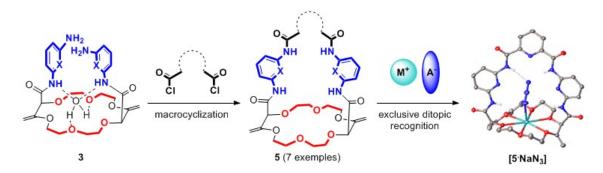
<u>A. Homberg</u>¹, D. Poggiali¹, S. K. Ray¹, J. Lacour¹*

¹Department of Organic Chemistry, University of Geneva

Previously, our group reported the synthesis of polyether macrocycles **1** by [3+6+3+6] condensations of α -diazo- β -ketoesters **2** and 1,4-dioxane under dirhodium catalysis at 1 *M* concentration.^[1] By reactions of **1** with aromatic amines under basic conditions, chiral crown ethers **3** can then be obtained in a single step by tandem amidation / olefin transposition.^[2] These compounds **3** are effective pH-insensitive nanosensors and ratiometric luminescent switches.^[3] For these and other applications, preparation of **1** in large quantities was required. Kinetics of decomposition of diazo **2** with various rhodium(II) catalysts and different amounts of dioxane were studied by *in situ* FT-IR monitoring. These mechanistic results showed the superior activity of Hashimoto-Ikegami-like catalyst **4**. Reaction conditions were optimized leading to a decrease of catalyst loading (down to 0.001 mol%) and a scale-up of the reaction up to 20 grams of **1** in a single batch.^[4]



Herein, we present in addition a new family of cryptands **5** readily synthesized in two steps from compounds **1**. Hosts **5** display a ditopic character towards sodium salts of linear anions in particular as demonstrated by ¹H NMR spectroscopic and solid state structural analysis.



[1] Walid Zeghida, Céline Besnard, Jérôme Lacour, *Angewandte Chemie International Edition* **2010**, 49, 7253-7256.

[2] Mahesh Vishe, Radim Hrdina, Amalia I. Poblador-Bahamonde, Céline Besnard, Laure Guénée, Thomas Bürgi, Jérôme Lacour, *Chemical Science* **2015**, 6, 4923-4928.

[3] a) Zdenka Jarolímová, Mahesh Vishe, Jérôme Lacour, Eric Bakker, *Chemical Science* **2016**, 7, 525-533; b) Stephan Sinn, Frank Biedermann, Mahesh Vishe, Alessandro Aliprandi, Céline Besnard, Jérôme Lacour, Luisa De Cola, *ChemPhysChem* **2016**, 17, 1829-1834.

[4] Daniele Poggiali, Alexandre Homberg, Thimothée Lathion, Claude Piguet, J. Lacour, ACS Catalysis **2016**, 6, 4877-4881.