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

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Previously, our group reported the synthesis of polyether macrocycles  $\bf 1$  by [3+6+3+6] condensations of  $\alpha$ -diazo- $\beta$ -ketoesters  $\bf 2$  and 1,4-dioxane under dirhodium catalysis at 1 M concentration. By reactions of  $\bf 1$  with aromatic amines under basic conditions, chiral crown ethers  $\bf 3$  can then be obtained in a single step by tandem amidation / olefin transposition. These compounds  $\bf 3$  are effective pH-insensitive nanosensors and ratiometric luminescent switches. For these and other applications, preparation of  $\bf 1$  in large quantities was required. Kinetics of decomposition of diazo  $\bf 2$  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  $\bf 4$ . 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  $\bf 1$  in a single batch. A single batch.

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 <sup>1</sup>H NMR spectroscopic and solid state structural analysis.

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