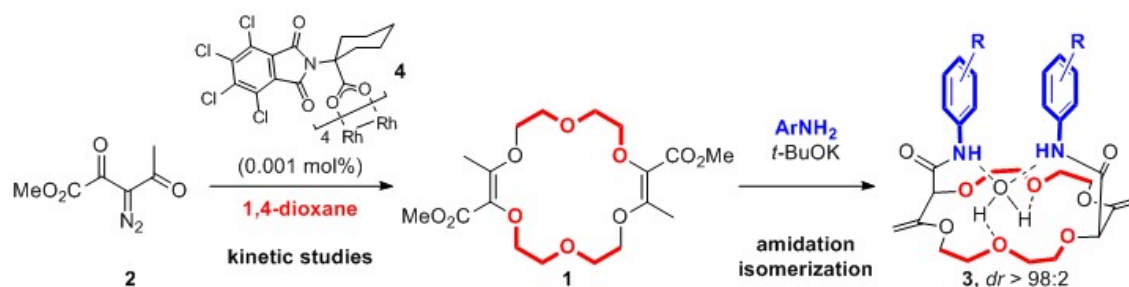


## Kinetics of Rh(II)-Catalyzed $\alpha$ -Diazo- $\beta$ -Ketoester Decomposition for Polyether Macrocycle Synthesis and Straightforward Access to Ditopic Cryptands

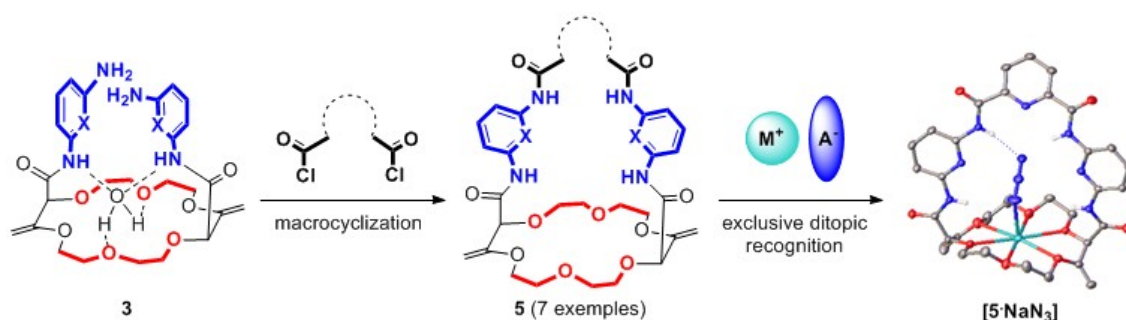
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Previously, our group reported the synthesis of polyether macrocycles **1** by [3+6+3+6] condensations of  $\alpha$ -diazo- $\beta$ -ketoesters **2** and 1,4-dioxane under dirhodium catalysis at 1 M concentration.<sup>[1]</sup> By reactions of **1** with aromatic amines under basic conditions, chiral crown ethers **3** can then be obtained in a single step by tandem amidation / olefin transposition.<sup>[2]</sup> These compounds **3** are effective pH-insensitive nanosensors and ratiometric luminescent switches.<sup>[3]</sup> 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.<sup>[4]</sup>



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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