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Efficient Synthesis of Anion Receptors Based on the Phenoxathiin Macrocycle

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Thiacalixarenes are macrocyclic compounds that are widely used in supramolecular chemistry. The main advantage of their skeleton is the possibility of its simple modifications. Being one of the easily accessible derivatives, phenoxathiin macrocycle is interesting due to its inherent chirality. However, wider utilization of this novel compound is problematic because of the lack of effective derivatization techniques.

We present the first and very efficient way how to introduce the amino groups to the upper rim of the macrocycle. It was performed by using the *ipso*-nitration of the fully S-oxidized macrocycle followed by selective reduction of nitro groups. The structures of most of the products were confirmed by X-ray crystallography of monocrystals.

Resulting amino derivative was further reacted with two selected isocyanates, providing the ureido-type receptors (Scheme 1). Their abilities to complex common anions were measured by NMR titration and unexpectedly high association constants were observed in all cases.

Scheme 1

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