

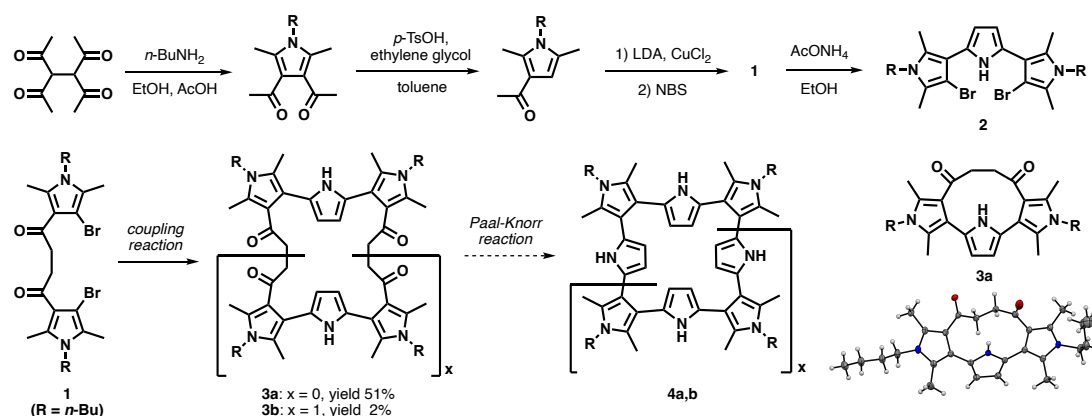
## Synthesis of Cyclo[n]pyrrole Derivatives Using Macrocyclic Oligoketone Precursors

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Cyclo[n]pyrroles<sup>1</sup> are oligopyrrole macrocycles that are known for  $n = 6-10$  with pyrrole  $\alpha$ - $\alpha$  linked pyrrolic subunits. To expand the scope of the synthetic access of cyclo[n]pyrrole derivatives especially for ring contracted analogues with different connectivity, we propose a novel precursor **1**, a synthon of terpyrrole derivative with  $\alpha$ - $\beta$  linkages.

Compound **1** was synthesized from 1,1,2,2-tetraacetylene in total 25% yield for 4 steps. Paal-Knorr pyrrole synthesis of **1** using ammonium acetate gave dibromo terpyrrole **2** in 60% yield, demonstrating that **1** can be used as a structurally flexible synthon of terpyrrole. Suzuki-Miyaura cross coupling reaction between **1** and 2,5-diborylpyrrole gave macrocyclic terpyrrole **3a** in 51% yield and the extended macrocyclic analogue **3b** was also isolated. Single crystal X-ray analysis of **3a** revealed an anti-periplanar conformation for the ethylene unit in 1,4-diketone. When final pyrrole formation reaction was conducted using similar reaction conditions to **2**, compound **3a** did not give target cyclo[4]pyrrole analogue, but the starting material was recovered, which was attributed to the increasing ring strain upon pyrrole formation. Suitable reaction conditions for the final pyrrole formation reaction with **3a** and **3b** are being explored.



**Figure 1.** Synthetic route of cyclo[n]pyrrole derivatives (**4a,b**) and X-ray crystal structure of cyclic terpyrrole with diketone units (**3a**).

1) J. Setsune, *Chem. Rev.*, **2017**, *117*, 3044.