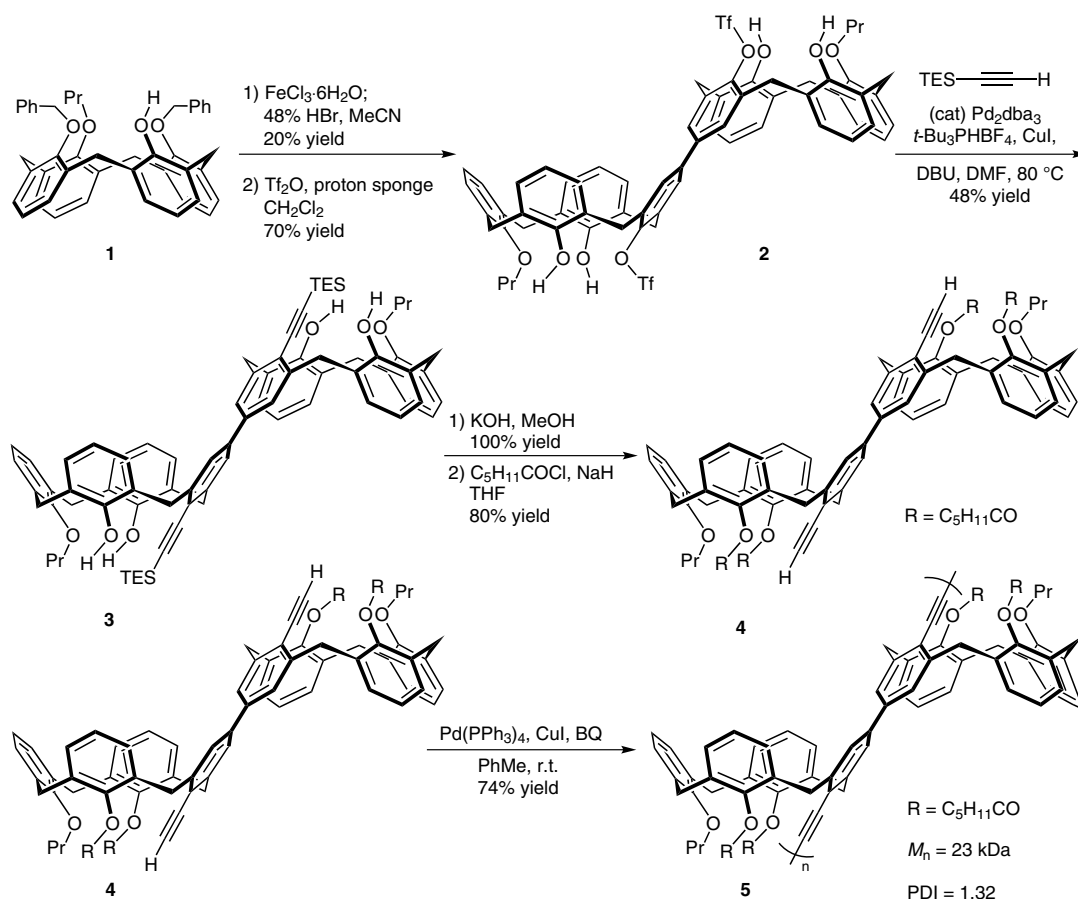


5,5'-Bicalixarene-Based Tubular Conjugated Polymer



Significance: A 5,5'-bicalixarene scaffold was incorporated into the linear backbone of a soluble conjugated polymer **5** via Glaser-type coupling. Monomer **4** synthesis relies on oxidative coupling of calixarene **1**, followed by deprotection and selective triflation. Next, the triflate was replaced with TES-acetylene, because direct cross-coupling of **3** with 1,4-diethynylbenzene failed. Deprotection of the alkyne and installation of solubilizing groups furnished the desired monomer in 5% overall yield.

Comment: Access to a closed (capsule-type) conformation in bicalixarenes greatly enhances complexation properties of the calixarene scaffold. Indeed, polymer **5** fluorescence ($\lambda_{\text{abs}} = 420 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$, $\Phi_{\text{FL}} = 0.37$) is efficiently quenched by NO vapor. Importantly, a brief application of low vacuum to remove NO completely restores the fluorescence, indicating that the complexation is reversible.